UNIVERSITY OF ALBERTA

EXTRACTION OF GOLD FROM A DOUBLE-REFRACTORY CONCENTRATE

BY

KAFUI NYAVOR

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled GOLD EXTRACTION FROM A DOUBLE-REFRACTORY CONCENTRATE submitted by KAFUI NYAVOR in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in MINERAL ENGINEERING.

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DEDICATION

Dedicated to **Nanna** and **Komla**

To Nanna I say, thanks for giving me the push

and to Komla

thanks for giving me the chance to .....

also to the memory of UNCLE NELSON.

ABSTRACT

Refractory behavior in gold ores and concentrate is generally attributable either to the occlusion of fine gold particles by sulfide minerals, or to preg-robbing activity and occlusion of gold or gold bearing minerals by carbonaceous materials. When an ore or concentrate exhibit refractoriness due to both phenomena, it is regarded as being "Double-Refractory". Acid pressure oxidation is currently being advocated as the most effective pretreatment method for refractory gold ores and concentrates. However, the refractoriness problems due to gold occlusion by sulfide mineralization have received much more research attention than those due to the presence of carbonaceous materials.

In this study, the effectiveness of sulfuric acid, nitric acid and hydrogen peroxide pressure oxidation and roasting on the cyanide extractability of gold from a double-refractory concentrate is presented. While over 90% of the sulfide content could be oxidized by acid pretreatment, only 65% was achieved by peroxide pressure oxidation. Carbon oxidation by both acid and peroxide pretreatments were less than 15%. Although the peroxide pretreatment resulted in much lower sulfur and carbon oxidation, it gave residues with decreased levels of preg-robbing activities and higher gold recoveries (83%) during subsequent cyanidation. The residual carbonaceous materials were found to be very active in terms of preg-robbing even after H_2SO_4 and HNO_3 pressure oxidation. These residues gave 65%-70% gold extraction during subsequent cyanidation. The refractoriness due to carbon preg-robbing activity was found to be predominant over the refractory phenomenon arising from the occlusion of gold particles by the sulfide mineralization.

It was found that only roasting pretreatment was capable of completely oxidizing the carbon and sulfide, leading to high gold extraction. Over 95% gold could be recovered after roasting the concentrate at 750°C. However, roasting resulted in sulfur dioxide and arsenic emission. In order to control the release of SO_2 and As_2O_3 gases during roasting, the effectiveness of a novel Lime Agglomeration Roast (LAR) pretreatment for sulfur

dioxide and arsenic trioxide gas emission control during roasting, and gold extraction efficiency during subsequent cyanidation was investigated.

This pretreatment resulted in the capture of 95% sulfur and 85% arsenic during roasting at optimum conditions of 700°C and Ca:S mole ratio of 1.5. Over 95% gold extraction was obtained during the cyanidation of the LAR residue. In addition to the removal of the noxious gases, the use of the LAR pretreatment process eliminated the need for additional lime for the pH adjustment of the cyanidation pulp. Since the anhydrite, calcium arsenite, and calcium arsenate formed during LAR pretreatment are stable, the cyanidation residues can be easily disposed in an environmentally acceptable manner. Similarly, the barren solutions obtained after gold recovery from the cyanidation leach liquor were found to contain very little arsenic and can therefore be disposed without further treatment.

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1. INTRODUCTION

Gold ores and concentrates are classified as refractory when a significant portion of the gold content cannot be extracted efficiently by conventional cyanidation, even after fine grinding [1, 2].

The refractory behavior of precious metal ores and concentrates is generally attributed to two main factors: the presence of carbonaceous materials which could cause preg-robbing activity during cyanidation [3-6], or occlude gold bearing minerals [7-9], and the occurrence of sulfide minerals which can occlude gold, thus reducing the access of lixiviants [10-14]. When the refractoriness is due to a combination of these two factors, the ore or concentrate is referred to as being "double-refractory". However, in most cases, one of the two factors responsible for the refractoriness will predominate during extraction.

In cases where the refractory nature of the ore is mainly due to preg-robbing by carbonaceous materials, several methods have been investigated to circumvent this problem. For example, the rejection of the carbonaceous material by flotation and/or the use of cyclones have been studied [15-17] but has not been very successful in most cases due of intimate association of the carbonaceous materials [15, 18, 19]. The deactivation of the carbonaceous material by chlorine or hypochlorite has been used to pretreat Carlin-type gold ores [20-22]. Furthermore, Carbon-in-Leach and Resin-in-Leach cyanidation processes have also been explored [23-25], based on the premise that the added adsorbent could adsorb gold from solution at a faster rate than the carbonaceous material in the ore or concentrate. Other studies have indicated that the in-leach processes do not give satisfactory gold extraction from carbonaceous ores due to the deactivation of the added adsorbents (i.e. activated carbon or resins) and the occlusion of gold particles by the carbonaceous ore materials [21, 23, 26].

When the refractoriness of the ore or concentrate is mainly due to occlusion of gold by sulfide minerals, sulfuric acid pressure oxidation is now believed to be one of the most

effective pretreatment methods, and is being used by a number of gold processing facilities [11, 27, 28]. Nitric acid pressure oxidation [29, 30] and microbiological pretreatment [31-35] have also been used successfully at laboratory and pilot plant scale for pretreating sulfide ores and concentrates.

In the presence of amorphous carbonaceous materials, the severe acid oxidation conditions employed for the pretreatment of refractory sulfidic gold ores and concentrates should theoretically be expected to oxidize most of the carbonaceous material content into acid soluble compounds [36], thereby reducing the preg-robbing activities. However, no significant information is available in the literature regarding the fate of carbonaceous materials during acid pressure oxidation. This is partly due to a number of factors, viz. the rarity of double-refractory gold ores and concentrates with significant amounts of carbonaceous materials, the emphasis on chlorination process for treatment of carbonaceous ores and concentrates (which is now becoming less effective, due to high chlorine consumption because of increasing carbon and sulfide content of carbonaceous ores being mined [37]), and the use of selective mining and processing to reject carbonaceous ores and concentrates which may contain a high content of gold values [4, 5, 38]. Like most mines, at Ashanti Gold Fields Corporation (Ghana), flotation cells and cyclones are used to concentrate the carbonaceous material to a special tailings pond in anticipation of possible future recovery of the gold values. The concentrates exhibit double-refractory characteristics and samples were obtained and used for this study.

The primary objectives of this thesis were:

(i) To study the effectiveness of three acid pressure oxidation methods for gold extraction from a double-refractory concentrate.

(ii) To investigate the extent of the carbon and sulfur content oxidation during pretreatment, and relate these to subsequent gold dissolution by cyanidation.

(iii) To determine which of the two major refractoriness phenomena is predominantly responsible for the poor gold recovery from the untreated concentrate.

(iv) To establish the optimum oxidation conditions leading to maximum gold extraction during subsequent cyanidation.

(v) To compare gold extraction using these pressure oxidation techniques with that obtained from the environmentally sensitive roasting treatment, and

(vi) To investigate the Lime Agglomeration Roast (LAR) pretreatment as a means of controlling sulfur dioxide and arsenic trioxide emissions during roasting.

Consequently, sulfuric acid, nitric acid, and hydrogen peroxide pressure oxidation, and Lime Agglomeration Roast (LAR) techniques were investigated in this study.

2. LITERATURE SURVEY

2.1 REFRACTORY GOLD ORES

Due to its noble or unreactive nature, gold occurs in nature mostly in metallic form, either by itself or alloyed with silver as electrum. The only other important gold minerals found in nature are gold or gold-silver tellurides [39]. However, there are numerous gold deposits around the world in which finely disseminated gold is found in association with pyrite, arsenopyrite, other arsenic sulfides [39] and/or carbonaceous materials [7-9]. Because of the fine nature of these gold particles and their dissemination in the sulfide and carbonaceous materials, it is generally impractical to grind the ore fine enough to liberate all the gold for amalgamation or cyanidation [40-42]. Such gold ores which do not respond well to the conventional cyanidation processes are generally called refractory gold ores and, therefore, require pretreatment before cyanidation can be effective [18, 43]. The free milling ores are generally those ores in which the gold is relatively coarse and amalgamable: the sulfide content is low and nonarsenical, oxidized compounds of bismuth and antimony are absent, and the gangue is substantially free from talc, clay and graphitic constituents [22].

The refractoriness of gold ores can be broadly distinguished as being of a chemical or physical nature. The chemical refractoriness is relatively rare and confined to three conditions:

1. Insoluble gold tellurides.
2. Ingredients of the ore that might decompose and react with cyanide (cyanicides).
3. Ingredients of the ore that consume oxygen.

The preponderant refractoriness of gold ores is of a physical nature and can be distinguished into five types, R1 to R5 as summarized in figure 1.

R1. Fine gold encapsulated or attached to host matter.

R2. Gold alloys.

R3. Gold coated with films (minerals films or films created during the treatment of the ore).

R4. Adsorbent materials (carbonaceous and/or clays) that rob dissolved gold from the pregnant solution (preg robbing materials).

R5. Decomposition of host minerals (sulfides can decompose and form cyanicides; sulfides, thiosulfites, arsenites and ferrous ions can consume oxygen; humic acid can interact with gold complexes) [44].

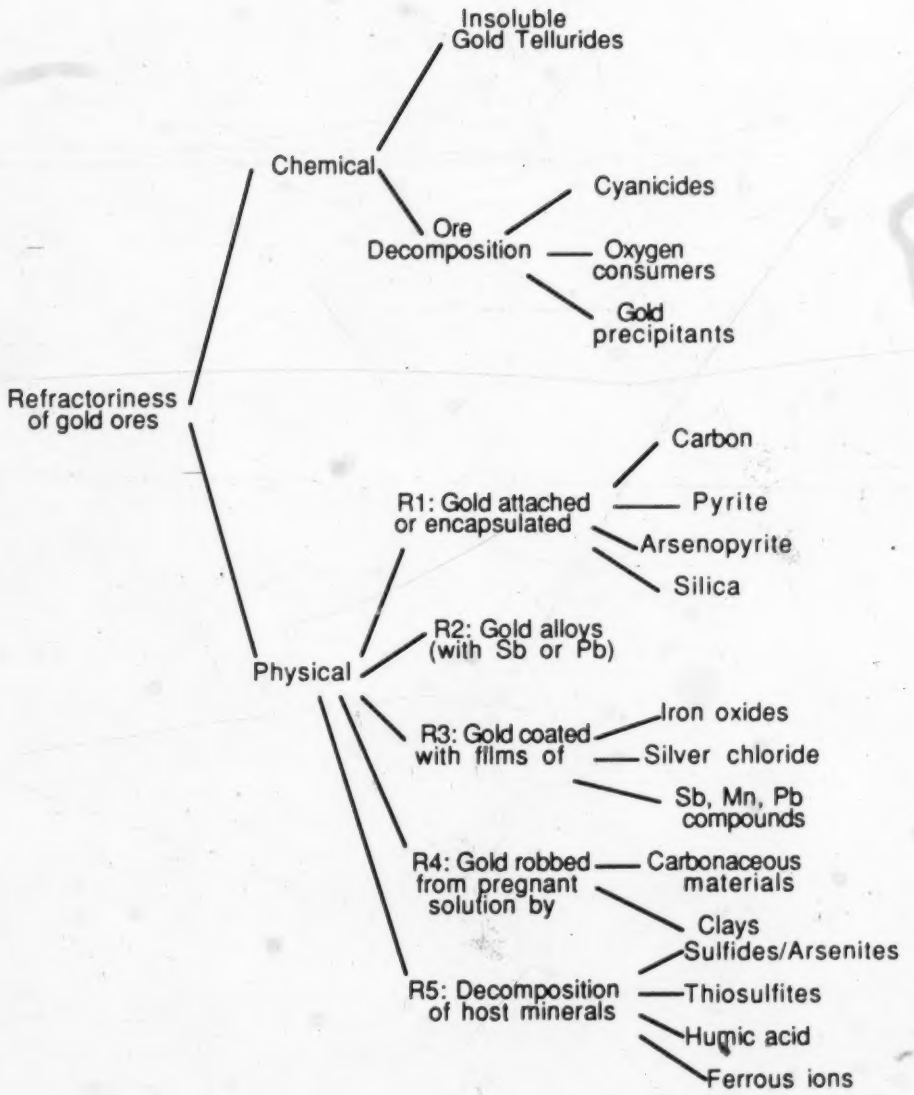

Figure 1. Classification of refractory gold ores

2.1.1 SULFIDE ORES

Sulfide ores are probably the largest group of refractory ores [8] with pyrite (FeS_2) and arsenopyrite (FeAsS) being the two most common gold carriers [45]. Occurrences of auriferous sulfides are quite common and have been described by many investigators [46-48]. Apart from pyrite and arsenopyrite, the other frequently encountered sulfide minerals are sphalerite, chalcopyrite, and pyrrhotite [49]. In other sulfide deposits, gold also occurs in other sulfides and sulfosalts such as galena, antimonite, and antimony-arsenic-bismuth-lead sulfosalts [38]. In several of these sulfide deposits, a significant portion of gold occurs in microscopic forms, probably as a lattice constituent of pyrite and arsenopyrite, so that even fine grinding fails to liberate the metal for recovery by cyanide leaching [2]. The exact nature of this "invisible" gold within the structure of the pyrite and arsenopyrite is currently the subject of intensive mineralogical investigations [50-52]. Studies of samples of ore from Cortez and Carlin showed major concentrations of gold occluded in spheroidal pyrite grains, and in smaller concentrations in thin rims around cubic grains. Two types of pyrites were identified, one is the spheroidal made of 0.5 to nearly 2 μm size crystallites that aggregate to form spheroidal particles of 20 to 30 μm sizes and the other type is the coarse euhedral pyrite of 10 to 50 μm in size which is cubic and has no internal porosity. The spheroidal pyrite is said to carry most of the gold [7]. In the Porgera gold-silver sulfide deposit in the central highlands of Papua New Guinea, most of the gold occurs in association with sulfides which are dominated by pyrite with lesser sphalerite and galena and minor chalcopyrite, marcasite, arsenopyrite and sulphosalts [11]. At the Prestea and Ashanti gold fields of Ghana, gold occurs predominantly in the sulfides (pyrite and arsenopyrite) and quartz with some amount in the carbonaceous matrix [53]. Gold telluride ores with or without silver dissolve very slowly or do not dissolve at all in cyanide solution and are also classified as refractory ores [8]. Generally, some sulfide minerals are also present in these telluride ores and, an oxidation pretreatment is necessary to oxidize the telluride and sulfide minerals before cyanidation [54].

There are also numerous arsenical gold deposits in which gold is predominantly associated with arsenopyrite. Out of the 115 gold districts reviewed by Schwartz [10], 45 reportedly had a direct relationship between gold and arsenopyrite with gold occurring in or on arsenopyrite. Some of the well known arsenical ore deposits are in Canada (Giant Yellowknife, Campbell Red Lake), in Soviet Union (Darasun), in South Africa (Barberton Area in Eastern Transvaal), France (Salsigne), Greece (Olympias), Brazil (Sao Bento), etc. [55]. Canada is said to have the most arsenical ore deposits [56]. These arsenopyrite ores require complete breakdown of the crystal structure of the host mineral by oxidation to liberate occluded gold [7].

2.1.2 CARBONACEOUS ORES

The mineralogy of carbonaceous gold ores is varied but for all such ores the most vital constituents are the carbon-containing components [53]. The ability of activated carbon to absorb gold from cyanide solution is well documented and has formed the basis of carbon-in-pulp technology [57, 58], thus, it is not surprising to find carbonaceous gold ore deposits in nature. The term "carbonaceous ores" has been loosely applied to those ores which contain a black graphite-like material which causes precipitation of the aurocyanide complexes [4]. In some mines the term "graphitic schist" has been used [59]; other terms include "carbonaceous shale" [60], and "black or carbonaceous slate" [61]. The carbonaceous gold ores represent a unique class of refractory precious metal ores in general. Not only does gold encapsulation by iron sulfide minerals occur, but these ores also contain organic matter which either directly or indirectly interferes with gold recovery by cyanidation [62]. Direct interference can be attributed to either occlusion of gold within organic matter or formation of a stable gold-carbon complex [21, 63]. A more common problem is indirect interference, whereby the aurocyanide complex formed during cyanidation is adsorbed by the native organic matter and is not available for recovery

[53, 64]. Information presented by many workers on the nature of gold in carbonaceous ores indicate that gold is present as finely disseminated microscopic to submicroscopic grains coated with carbon [9, 53, 65].

Carlin [66] and Jerritt Canyon [24] represent two major deposits of this category. One of the dominant characteristics of the unoxidized, carbonaceous Carlin-type gold ores is that gold is not generally visible even under optical microscopes at the highest possible magnification due to the metal's high degree of dissemination and low average bulk concentration [67]. In addition to carbonaceous material, the Carlin type Nevada ores contain up to three per cent pyrite [52]. In the Ghanaian carbonaceous ore, the carbonaceous material is intimately associated with quartz, sericite, chlorite, carbonates and some amount of sulfide [59]. The carbonaceous matter in the gold bearing carbon seams in the Witwatersrand ores of South Africa does not interfere with cyanidation [68]. It is described as a complex, solid, and solvent insoluble, polymer-like substance, containing mainly hydrocarbons and some organic sulfur and oxygen compounds [69]. At the McIntyre Porcupine Mine, the carbonaceous matter was identified as a disordered graphite structure with small crystal size in the range of 0.02 to 0.05 μm [4].

Attempts to isolate and characterize the carbonaceous materials in gold ores have only been partly successful [3, 53, 69, 70]. The material is said to be very similar to an activated carbon [4] but, despite the considerable amount of research which has been completed, the mechanics of this process are still insufficiently clear [3]. Laboratory investigations by the U.S. Bureau of Mines on carbonaceous ores from Carlin showed that they contained:

1. An activated carbon component capable of adsorbing gold chloride or gold chloride complexes from solution;

2. A mixture of high molecular weight hydrocarbons usually associated with activated carbon components; and

3. An organic acid, similar to "humic acid" containing functional groups capable of interacting with gold complexes to form organic gold compounds [70].

2.2 PRETREATMENT OF REFRACTORY GOLD ORES AND CONCENTRATES

To render refractory gold ores and concentrate amenable to cyanidation, prior treatment by oxidation is usually required to decompose the crystal structure of the host minerals and thereby liberate gold [12]. In practice, refractory ores are submitted, as a rule, to some form of oxidation pretreatment before cyanidation [44]. Pyrometallurgical and hydrometallurgical methods have been practised or proposed as oxidation pretreatment processes for refractory gold [71]. Figure 2 shows some potential pretreatment methods for refractory gold ores and concentrates [44].

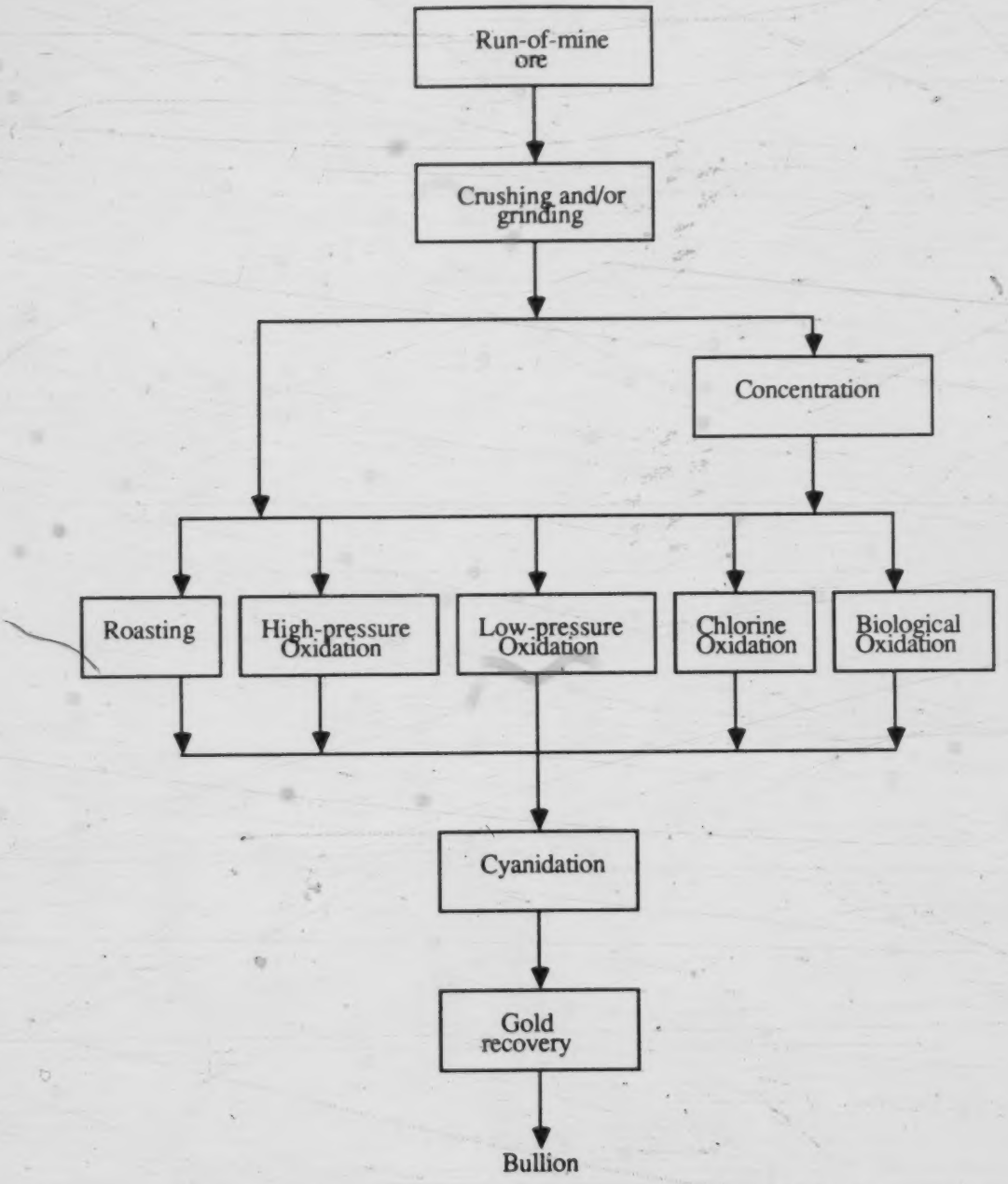

Figure 2. Oxidative pretreatment alternatives for refractory gold ores.

2.2.1 ROASTING

Roasting is the oldest process for pretreating refractory ores and has been used to process pyrite and arsenopyrite gold ores and concentrates since as early as 1925 in Australia, Canada, South Africa, and the United States [39]. Roasting was industrially applied on a large scale even when chlorination was the established leaching method for gold ores (before cyanidation) [44]. The Campbell Lake Mines, the Giant Yellowknife Mines and the Kerr Addison Mines all located in Canada used roasting to pretreat arsenical sulfide gold ores prior to cyanidation [22].

Roasting has the objective of liberating any gold particles encapsulated or attached to sulfides, arsenopyrites, or carbon, and of destroying carbonaceous material and any potential cyanicides. Hence, a porous, fluffy calcine which neither encapsulates nor coats the gold particles is the desirable product of roasting [44]. Over the decades the single- and multiple-hearth roaster have been replaced with the fluidized-bed roaster [38]. Fluidized-bed roasting is still the most commonly used preoxidation process for treating large quantities of pyritic, arsenopyritic, and telluride concentrates [22]. For arsenical ores, two-stage roasting is commonly used [39, 72]. The first stage, maintained at a low temperature (350-450°C) and oxygen-deficient conditions, helps in recovering the arsenic as volatile As_2O_3 which is condensed, collected and sold. The second stage, operated at a higher temperature (450-700°C) with excess oxygen, helps in near complete removal of sulfur [72]. It has been suggested that if arsenic is oxidized to nonvolatile As_2O_5 instead of volatile As_2O_3, iron or calcium arsenates are formed which adversely affect the extraction of gold and silver [73].

Microwave irradiation has also been used to decompose refractory concentrates containing pyrite and arsenopyrite. It was observed that the overall chemistry of both microwave calcination and conventional thermal roasting of the concentrate was essentially the same [74]. It has been found that pyrite roasting becomes difficult in the presence of carbon and other metal sulfides. A higher temperature (generally above 650°C) is needed

to oxidize the carbon, but the presence of other sulfides such as copper, cobalt, nickel, or zinc sulfides also lead to the formation of ferrites at higher temperatures. Gold and particularly silver trapped in the ferrite grains, is not accessible to cyanide solution. A lower temperature (generally below 600°C), on the other hand, results in incomplete oxidation, particularly that of organic matter which results in preg-robbing [75]. A study of the oxidation kinetics for carbon in a mixture with pyrite (FeS_2) and arsenopyrite (FeAsS) showed that even at 1100°C, in order to completely oxidize the carbon, a roasting period three times longer than that for oxidizing the pyrite and arsenopyrite was required. It was observed that due to lower oxidation rate, carbon remains in the cinders until the very last traces of sulfide decomposition [76]. Other studies on the roasting characteristics of carbonaceous gold ores have shown that the carbon in the ore has to be oxidized to a minimum value before any appreciable oxidation of the sulfur occurs. It is suggested that the sulfide minerals are encapsulated within the carbonaceous matrix and until the carbonaceous materials are completely oxidized, oxygen have no chance of coming in contact with sulfur to oxidize it [9]. Temperature control during roasting of carbonaceous ores is also critical to ensure that oxidation of carbonaceous materials proceeds without the deleterious morphological effects brought on by higher temperatures [77], and to avoid "flash" roasting, i.e. the fusion of the calcines and the "re-lockup" of the gold micrograins [44].

CHEMISTRY OF ROASTING PROCESS

A multitude of chemical reactions are possible in roasting, depending on the host mineral(s) causing the refractoriness, the excess of air, and the prevailing temperature during roasting. The main reactions of roasting of pyritic and arsenopyritic minerals are strongly exothermic, and the gold-containing particles are sites of heat generation [44]. Arsenic, sulfur and many of their compounds have significant vapor pressures at the temperatures encountered during the roasting of sulfide concentrates, 450°C to 650°C.

The pyrite and arsenic sulfides present in the concentrate or in the vapor phase decompose at these high temperatures to yield elemental arsenic and sulfur vapors which are easily oxidized by air. The two oxidation products, As_2O_3 and SO_2, leave the roaster as off gases along with nitrogen and any unused oxygen [39]. Studies with arsenopyrite suggest that it decomposes easily at about 430°C to 530°C to arsenic vapor and pyrrhotite (FeS). The availability of oxygen in excess of that required to oxidize arsenic and sulfur, oxidizes pyrrhotite (FeS) to magnetite (Fe_3O_4) and to hematite (Fe_2O_3) [78]. Pyrrhotite (FeS) is oxidized to Fe_3O_4, Fe_2O_3 or $Fe_2(SO_4)_3$ depending upon the oxygen partial pressure, SO_2 partial pressure, and temperature. While the presence of magnetite has been considered desirable by some operations [73], hematite is the usual product of roasting.

In the absence, or deficiency, of air, decompositions of sulfides and arsenides are possible [44].

$$FeS_2 \quad \text{----> } FeS + S \qquad (1)$$

$$4FeAs_2 \quad \text{----> } Fe_4As + 7As \qquad (2)$$

$$FeAsS \quad \text{----> } FeS + As \qquad (3)$$

$$2FeAsS + 2FeS_2 \quad \text{----> } 4FeS + As_2S_2 \qquad (4)$$

Depending on the excess of air and the prevailing temperature, the following oxidation reactions can be expected, among others during the thermal decomposition of pyrite and arsenopyrite, producing sulfur dioxide, arsenic trioxide, and iron oxides (hematite and/or magnetite) as main products.

$$4FeS_2 + 11\,O_2 \quad \text{----> } 2Fe_2O_3 + 8SO_2 \qquad (5)$$

$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2 \quad (6)$$

$$3FeS_2 + 8O_2 \longrightarrow Fe_3O_4 + 6SO_2 \quad (7)$$

$$3FeS + 5O_2 \longrightarrow Fe_3O_4 + 3SO_2 \quad (8)$$

$$FeS_2 + O_2 \longrightarrow FeS + SO_2 \quad (9)$$

$$FeS_2 + 3O_2 \longrightarrow FeSO_4 + SO_2 \quad (10)$$

$$FeAsS + 3O_2 \longrightarrow FeAsO_4 + SO_2 \quad (11)$$

$$2SO_2 + O_2 \longrightarrow 2SO_3 \quad (12)$$

$$4As + 3O_2 \longrightarrow 2As_2O_3 \quad (13)$$

$$2As_2S_2 + 7O_2 \longrightarrow 2As_2O_3 + 4SO_2 \quad (14)$$

$$As_2S_2 + O_2 \longrightarrow As_2O_5 \quad (15)$$

$$2FeAsO_4 \longrightarrow Fe_2O_3 + As_2O_5 \quad (16)$$

$$FeO + SO_3 \longrightarrow FeSO_4 \quad (17)$$

$$4Fe_3O_4 + O_2 \longrightarrow 6Fe_2O_3 \quad (18)$$

2.2.2 PRESSURE OXIDATION

In recent years there has been a considerable interest in pressure hydrometallurgy as an alternative to roasting for liberating gold from sulfides [28]. Pressure hydrometallurgy has been used extensively to conduct the three main elements of extractive metallurgy: metals extraction, metals recovery, and waste control [79]. Pressure oxidation and leaching are attaining an expanding role, particularly in the treatment of sulfide and arsenide containing materials such as ores and flotation concentrates, smelter mattes and chemical precipitates [80]. The aim of aqueous pressure oxidation of refractory gold bearing sulfides is to liberate gold. The applicability of pressure oxidation for rendering a wide range of refractory gold ores and flotation concentrates more amenable to cyanidation was demonstrated by American Cyanamid Co. [81].

Oxidation of sulfides from a thermodynamic point of view is feasible over the entire pH range. Pressure oxidation can therefore be conducted in either alkaline or acidic media but it is only the latter approach that has been promoted to the level of commercial operation [82].

Presently, pressure oxidation appears to be the best established approach to oxidation of refractory ores. It appears to offer a number of advantages over roasting, both from the processing and environmental points-of-view. Strict control is not a critical factor in the operation of a pressure leach plant, as it is in the case of a roasting facility [1, 2, 71]. Pressure leaching is claimed to almost always render the refractory material amenable to cyanidation and to consistently give higher gold recoveries [71]. Ores and concentrates alike can be treated by pressure oxidation with no air pollution by SO_2 or arsenic emissions [71, 88].

2.2.2.1 SULFURIC ACID PRESSURE OXIDATION

Sulfuric acid pressure oxidation is currently considered the most effective for pretreating refractory gold ores and concentrates, due to a number of metallurgical and environmental advantages [2]. Acid pressure oxidation employs temperatures above the melting point of sulfur (119°C), preferably above 170°C and high oxygen overpressures up to 2000 kpa [12]. Gold extractions have been found to increase from the range of 6 to 70% prior to oxidation, to the range of 85 to 98% after acid pressure oxidation [1, 2, 28].

CHEMISTRY OF SULFURIC ACID PRESSURE OXIDATION

The pertinent process chemistry of the elevated temperature acid pressure oxidation of arsenopyrite and pyrite in an aqueous medium is presented below [1, 82]. The major reactions involve the total oxidation of the sulfidic sulfur to the sulfate form.

$$4FeAsS + 11\,O_2 + 2H_2O \longrightarrow 4HAsO_2 + 4FeSO_4 \quad (1)$$

$$2FeS_2 + 7\,O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \quad (2)$$

$$2Fe_7S_8 + 31\,O_2 + 2H_2O \longrightarrow 14FeSO_4 + 2H_2SO_4 \quad (3)$$

$$MS + 2\,O_2 \longrightarrow MSO_4 \quad \text{where M is Pb, Zn.} \quad (4)$$

The divalent iron and the trivalent arsenic are oxidized to their respective ferric and arsenate states.

$$4FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \quad (5)$$

$$2HAsO_2 + O_2 + 2H_2O \longrightarrow 2H_3AsO_4 \quad (6)$$

Under mildly oxidizing conditions (100° to 160°C) and in the presence of relatively large amounts of sulfuric acid and ferric sulfate, elemental sulfur may be formed as the preferred, or as an intermediate, product of the oxidation of arsenopyrite, pyrrhotite, and base metal sulfides [82].

$$4FeAsS + 5O_2 + 4H_2SO_4 \longrightarrow 4HAsO_2 + 4FeSO_4 + 4S^o + 2H_2O \quad (7)$$

$$2FeAsS + 7Fe_2(SO_4)_3 + 8H_2O \longrightarrow 16FeSO_4 + 2H_3AsO_4 + 5H_2SO_4 + 2S^o \quad (8)$$

$$2Fe_7S_8 + 14H_2SO_4 + 7O_2 \longrightarrow 14FeSO_4 + 16S^o + 14H_2O \quad (9)$$

$$Fe_7S_8 + 7Fe_2(SO_4)_3 \longrightarrow 21FeSO_4 + 8S^o \quad (10)$$

$$2MS + 2H_2SO_4 + O_2 \longrightarrow 2MSO_4 + 2S^o + 2H_2O \quad (11)$$

$$MS + Fe_2(SO_4)_3 \longrightarrow MSO_4 + 2FeSO_4 + S^o \quad (12)$$

In a few instances, elemental sulfur has also been identified as an oxidation product of pyrite.

$$FeS_2 + 2O_2 \longrightarrow FeSO_4 + S^o \quad (13)$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2S^o \quad (14)$$

The formation of elemental sulfur is favoured only during the initial stages of the reaction of pyrite, at relatively low temperatures (90 to 120°C), and at high acidities. Molten sulfur (i.e. at temperatures above 120°C) is an effective collector of various sulfides and is able to collect gold. Elemental sulfur is therefore undesirable for a number of reasons, including: occlusion of unreacted sulfides, which prevents complete oxidation; occlusion of gold particles, which hinders extraction during cyanidation; increased consumption of cyanide during cyanidation; and increased consumption of oxygen during cyanidation. Oxidation of the sulfides is, therefore, conducted at temperatures in excess of 160°C, and preferably higher than 175°C, to promote complete oxidation of the sulfides to sulfates and to oxidize any elemental sulfur formed as an intermediate product [1, 28].

$$2S^{o} + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 \qquad (15)$$

Under pressure oxidation conditions, a significant portion of the iron and arsenic are precipitated as ferric arsenate.

$$Fe_2(SO_4)_3 + 2H_3AsO_4 \longrightarrow 2FeAsO_4 + 3H_2SO_4 \qquad (16)$$

Some of the ferric sulfate can also be hydrolyzed and precipitated as hematite, as a basic ferric sulfate, or as hydronium jarosite.

$$Fe_2(SO_4)_3 + 3H_2O \longrightarrow Fe_2O_3 + 3H_2SO_4 \qquad (17)$$

$$Fe_2(SO_4)_3 + 2H_2O \longrightarrow 2Fe(OH)SO_4 + H_2SO_4 \qquad (18)$$

$$3Fe_2(SO_4)_3 + 14H_2O \longrightarrow \underset{\text{hydronium jarosite}}{2(H_3O)Fe_3(SO_4)_2(OH)_6} + 5H_2SO_4 \qquad (19)$$

The nature and composition of the precipitated iron species depend on parameters such as temperature, total sulfate levels, acidity, pulp density, composition and grade of the sulfides, and the nature and quantity of gangue components. In several instances, a complex species containing iron, arsenic and sulfur in the approximate molar ratio of 2:1:1, resembling sarmientite or bukovskyite, $Fe_2(AsO_4)(SO_4)OH.nH_2O$, has been identified in the oxidation products. In the presence of potassium and sodium, released by the dissolution of some of the gangue components, hydrolysis of at least a portion of the ferric sulfate to the corresponding jarosite may be expected [1].

$$3Fe_2(SO_4)_3 + K_2SO_4 + 12H_2O \text{ ----> } \underset{\text{potassium jarosite}}{2KFe_3(SO_4)_2(OH)_6} + 6H_2SO_4 \qquad (20)$$

A number of other metals such as silver, mercury, and lead are also precipitated as jarosites either through substitution for the potassium, sodium, or hydronium ions, or through formation of solid solutions in the jarosites precipitated [28,82]. Figure 3 shows a typical flow diagram for pressure oxidation of sulfide refractory ore under acidic conditions [44].

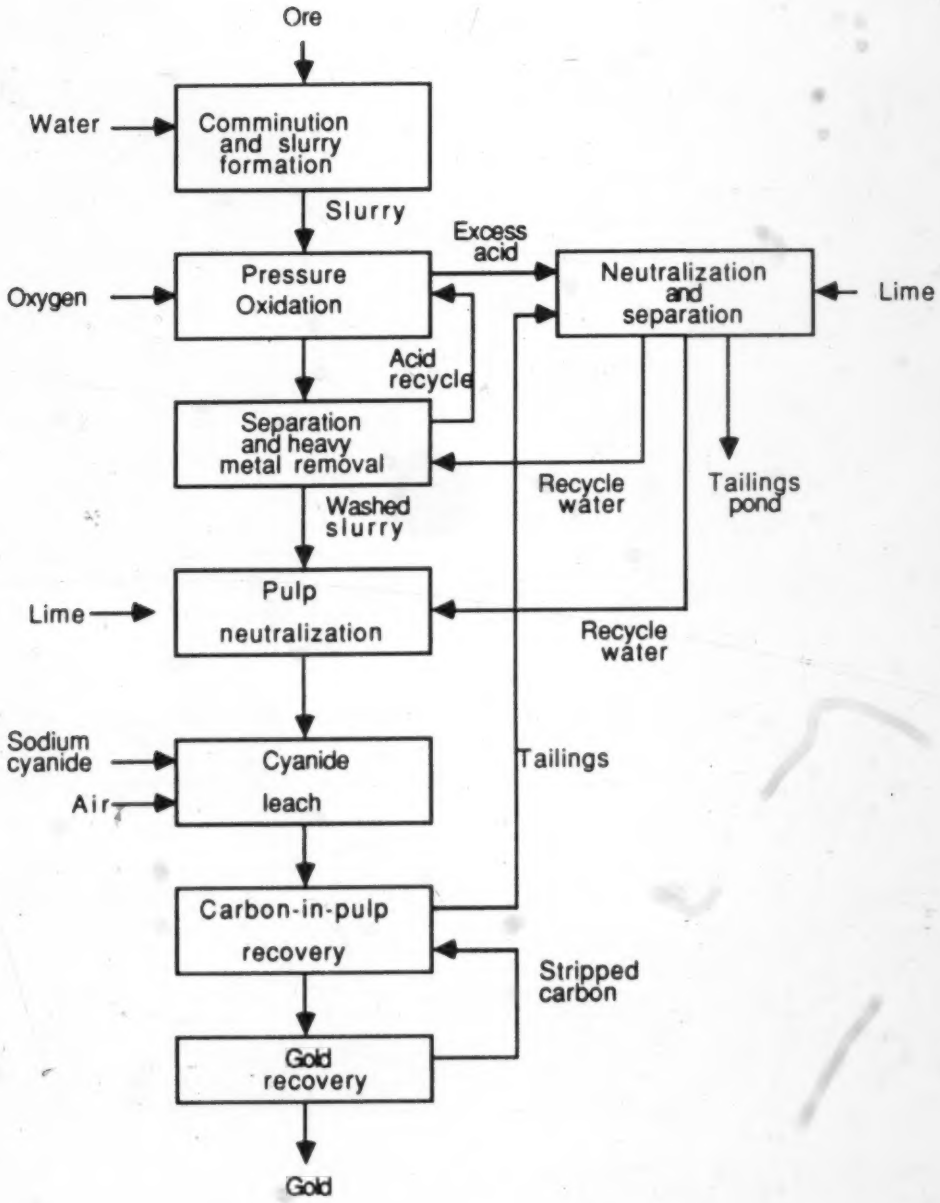

Figure 3. Pressure oxidation of sulfide refractory ore in acidic conditions with subsequent neutralization of the pulp.

2.2.2.2 NITRIC ACID PRESSURE OXIDATION

Nitric acid based processes have recently been reported for treating sulfidic refractory gold ores [29, 30]. The Arseno and Nitrox processes utilize nitric acid chemistry for the treatment of refractory gold ores [29, 83] but differ considerably in the engineering design [71]. The Nitrox process utilizes air at atmospheric pressure [83-85] and the Arseno process utilizes pressurized oxygen [29, 30, 85-87]. The processes have been operated on a continuous pilot scale with both low sulfide whole ore and high sulfide arsenopyrite concentrate. The process conditions which were used resulted in no elemental sulfur formation so that subsequent cyanidation could be performed efficiently and economically [88].

The Arseno process has been conducted at pressures between 100 kpa for ores and 700 kpa for high sulfide concentrates. Pyrite decomposition is generally complete within 15 minutes of oxidation [30]. Pyrite will react with acidic nitric solutions over a wide range of temperatures. Similarly, arsenopyrite will react with nitric acid over a wide temperature range. The choice of process temperature depends largely on the nature of feed being treated [30]. The benefit from treating concentrates at high temperature relates to the elimination of elemental sulfur. At temperatures below 180°C other workers attempting to develop processes for the treatment of sulfide concentrates have been plagued by the formation of elemental sulfur [28, 82]. While pyrite forms only minor elemental sulfur at 100°C, arsenopyrite yields up to 20% of its sulfide sulfur as elemental sulfur and pyrrhotite yields 100% elemental sulfur. It has been demonstrated that by operating the Arseno process at 195°C a sulfide concentrate containing 60% sulfide as arsenopyite and pyrrhotite produced no elemental sulfur [88].

The Nitrox process also has been operated at atmospheric pressure, 90°C and retention times of one to two hours. Several ores and concentrates have responded favorably to the Nitrox process with gold recoveries improving from 30% to over 90% [84].

CHEMISTRY OF NITRIC ACID PRESSURE OXIDATION

Although nitric acid chemistry is very complex, and involves a number of individual reactions, the oxidation is viewed in terms of a few overall reaction steps. The oxidation of pyrite by nitric acid can be represented by the following equation:

$$2FeS_2 + 10HNO_3 \text{ ----> } Fe_2(SO_4)_3 + H_2SO_4 + 10NO + 4H_2O \quad (1)$$

The reaction is very rapid, resulting in complete pyrite decomposition within several minutes. In practice, nitric acid is not an active reactant for sulfide mineral oxidation. Intermediate products of the reduction of nitric acid, primarily nitrous acid, are the active species [88]. In reaction (1), the nitric acid is reduced to nitric oxide which is released into the gas phase. Oxygen is supplied to the gas phase and reacts with the nitric oxide as shown by equation (2) [30].

$$6NO + 3O_2 \text{ ----> } 6NO_2 \quad (2)$$

The nitrogen dioxide (NO_2) which is formed is very rapidly absorbed by water:

$$6NO_2 + 2H_2O \text{ ----> } 4HNO_3 + 2NO \quad (3)$$

If these last two reactions are assumed to go to completion, the overall reaction becomes:

$$4NO + 3O_2 + 2H_2O \text{ --> } 4HNO_3 \quad (4)$$

The nitric acid is therefore regenerated as long as oxygen is present. If the stoichiometric quantity of oxygen required for the pyrite oxidation is provided, the net reaction becomes:

$$4FeS_2 + 15O_2 + 2H_2O \text{ ----> } 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (5)$$

The reaction is therefore the oxidation of the pyrite by oxygen with nitric acid acting as a catalyst. The oxidation of arsenopyrite by nitrous acid can also be represented by a similar set of reactions.

$$2FeAsS + H_2SO_4 + 28HNO_3 \text{ ----> } Fe_2(SO_4)_3 + 2H_3AsO_4 + 28NO(g) + 12H_2O \quad (6)$$

Free acid is essential for the formation of nitrous acid and its reduction to nitric oxide. In order for the oxidation reactions to continue the solution pH must be maintained below 1.7 [86].

While the oxidation of pyrite results in the production of acid, if there are significant acid consumers present in the ore or concentrate, additions of sulfuric acid may be required. In the case of arsenopyrite the oxidation reactions result in a consumption of acid so that an outside source of acid is required [88]. The regeneration of the nitric acid can be carried out concurrent with the sulfide oxidation reactions through the introduction of gaseous oxygen into the reaction vessel. Alternatively, the nitric oxide can be removed from the reaction vessel and regenerated externally [87]. It is practical to regenerate the nitric acid externally when treating a low-sulfide ore because the ratio of nitric acid to solids is very low. When treating a high-sulfide concentrate, oxygen must be supplied to the reaction vessel so that a sub-stoichiometric amount of nitric acid will result in complete sulfide oxidation [88]. Figure 4 shows a typical flowsheet of the Nitrox process [85].

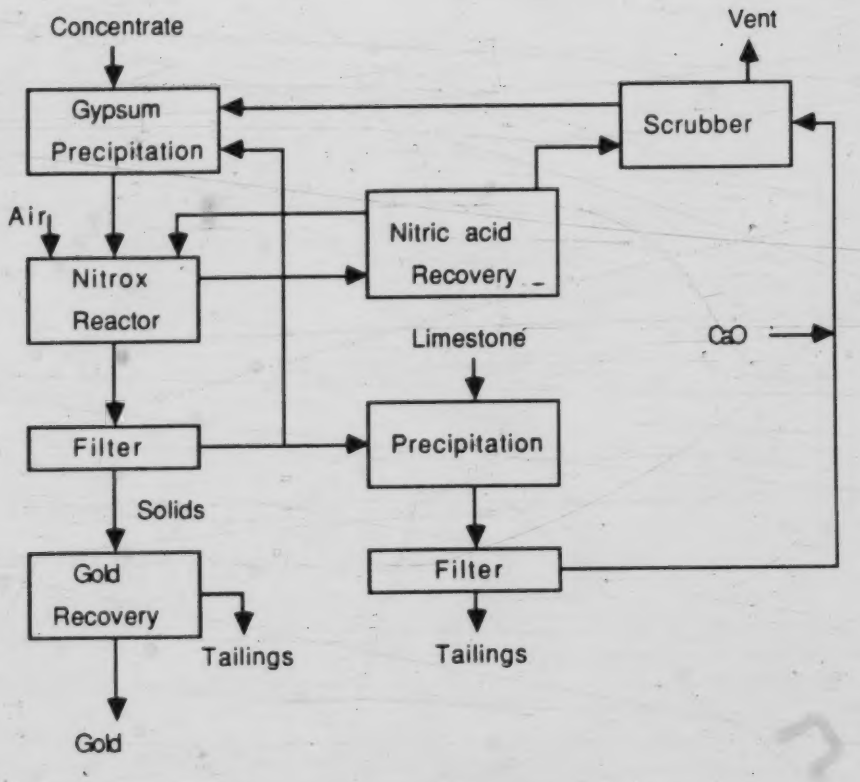

Figure 4. Flowsheet of Nitrox process for pretreatment of refractory gold concentrate.

2.2.2.3 ALKALINE PRESSURE OXIDATION

Alkaline pressure oxidation using NaOH and oxygen was proposed in the late 1950's [89] for treating arsenic sulfide ores, and used commercially for treating a cobalt-nickel arsenic ore [90]. This technique is currently being employed at the Barrick Mercur Gold Mine, Utah [91]. The alkaline pretreatment utilizes NaOH, low temperatures and pressures, and gold extraction is enhanced after the pretreatment of sulfide ores [92]. The U.S Bureau of Mines also investigated the use of the alkaline (NaOH) oxidative leaching procedure for treating gold-bearing arsenopyrite (FeAsS) ore, in an effort to develop an efficient and environmentally safe metallurgical process [93]. Alkaline pressure pretreatment yields a residue basically composed of iron oxide, while the sulfur and arsenic contents of the refractory minerals are solubilized completely as sodium sulfate and arsenate salts [71]. The residue from the alkaline process does not require washing or neutralization before cyanidation but those from the acid process necessitate thorough washing and residual acid neutralization prior to cyanidation for gold recovery. Also, ores containing high carbonates will result in high acid consumption and silver recovery from the acid procedure is usually poor because during oxidation silver has the propensity to form insoluble jarosites [93]. The development of the alkaline pressure leach route has been hampered due to the high reagent cost (NaOH), and the problem of arsenic disposal as Na_3AsO_4 [71]. Alkaline autoclaving using sodium carbonate is claimed to have been used to improve gold recovery by passivating organic carbon and preventing readsorption of gold cyanide complex on a laboratory scale [43]. Figure 5 shows a typical alkaline pressure oxidation flowsheet for treating refractory gold ores [92].

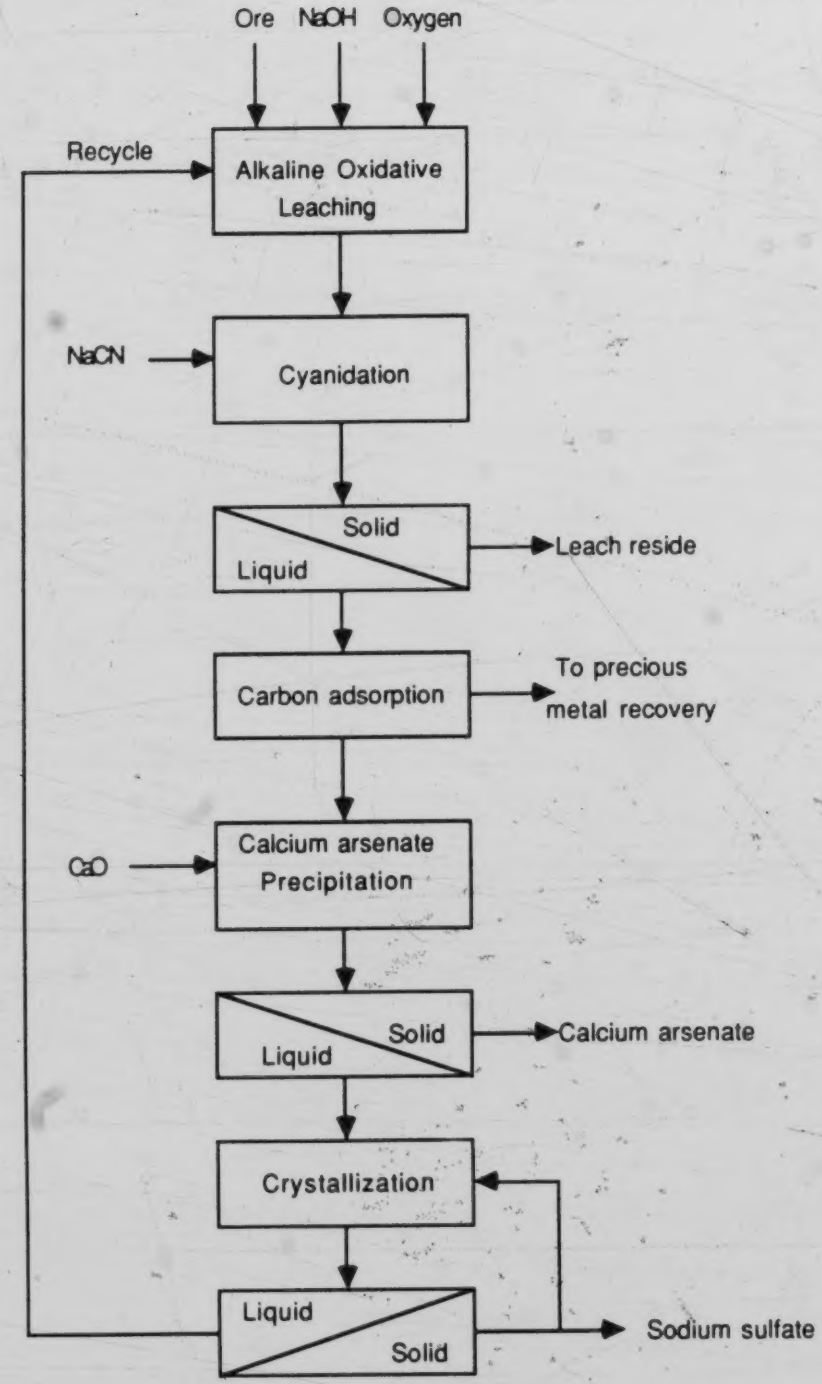

Figure 5. Alkaline pressure oxidation flowsheet for treating refractory gold ores.

2.2.3 MICROBIOLOGICAL OXIDATION PRETREATMENT

Bacterial leaching has been proposed as an alternative to roasting and pressure oxidation to break down the refractory sulfides so that the gold is liberated for recovery [94]. Thiobacillus ferrooxidans and Thiobacillus thiooxidans are the two major microorganisms contributing to the bacterial leaching of metals from sulfide ores [95]. The bioxidation process is principally based on the capability of the mesophilic bacterium Thiobacillus Ferrooxidans for chemolithophic growth in acidic environment. This organism obtains energy from the oxidation of ferrous iron and reduced sulfur compounds. It is therefore able to oxidize gold-bearing sulfide minerals such as pyrite and arsenopyrite [96]. It was the isolation from acid mine drainage and subsequent characterization of Thiobacillus Ferrooxidans that demonstrated the essential role of bacterial iron oxidation in the leaching of minerals and the pollution caused by acid mine drainage [97]. The major characteristic of bacterial leaching reactions is that they are autocatalystic, i.e. the bacteria are themselves a product of the reaction [96]. While gold recovery from sulfide ores and concentrates is enhanced following microbial pretreatment, it has little effect on the preg-robbing characteristics of carbonaceous gold ores [63]. Bioleaching ores and concentrates with high sulfur content presents a problem, since the reactions enhanced by bacteria are exothermic and the bacteria are inactivated at temperatures higher than 40°C [44]. Therefore, a microbial oxidation system for sulfide ores and concentrates has to be equipped with a cooling system, which increases the operating cost [44].

CHEMISTRY OF MICROBIOLOGICAL OXIDATION

The main reactions that take place during the bacterial leaching of sulfides can be represented by the equations listed below. For the oxidation of pyrite, equations (1-5) demonstrate the ability of Thiobacillus ferrooxidans to oxidize the mineral directly, oxidize the ferrous ions produced by mineral oxidation or by the chemical reduction of ferric iron, and oxidize sulfur produced by ferric ion oxidation of the mineral.

$$2FeS_2 + 7O_2 + 2H_2O \text{ --Bacteria--> } 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$2FeS_2 + 2H_2SO_4 + O_2 \text{ --Bacteria--> } 2FeSO_4 + 4S^o + 2H_2O \quad (2)$$

$$4FeSO_4 + 2H_2SO_4 \text{ --Bacteria--> } 2Fe_2(SO_4)_3 + 2H_2O \quad (3)$$

$$2S^o + 3O_2 + H_2O \text{ --Bacteria--> } 2H_2SO_4 \quad (4)$$

$$FeS_2 + Fe_2(SO_4)_3 \text{ --Bacteria--> } 3FeSO_4 + 2S^o \quad (5)$$

The overall oxidation of pyrite by the bacteria can be expressed by equation (6) [98].

$$4FeS_2 + 15O_2 + 2H_2O \text{ --Bacteria--> } 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (6)$$

Oxidation of arsenopyrite can be represented by the following reaction, in which pentavalent arsenic is formed:

$$4FeAsS + 13O_2 + 6H_2O \text{ --Bacteria--> } 4H_3AsO_4 + 4FeSO_4 \quad (7)$$

The ferrous sulfate produced by this reaction is then oxidized according to equation (3) to produce ferric sulfate. Trivalent arsenic may be formed as an intermediate product, followed by oxidation of the trivalent arsenic by ferric iron to the pentavalent form.

$$4FeAsS + 11O_2 + 2H_2O \text{ ----> } 4HAsO_2 + 4FeSO_4 \quad (8)$$

$$HAsO_2 + Fe_2(SO_4)_3 + 2H_2O \rightarrow H_3AsO_4 + 2FeSO_4 + H_2SO_4 \quad (9)$$

Oxidation of arsenopyrite by ferric sulfate may also take place.

$$2FeAsS + 2Fe_2(SO_4)_3 + 3H_2O + 5/2\,O_2 \rightarrow 2H_3AsO_4 + 6FeSO_4 + 2S^o \quad (10)$$

In the presence of ferric iron in solution, ferric arsenate may be formed from pentavalent arsenic and precipitated [99].

$$2H_3AsO_4 + Fe_2(SO_4)_3 \rightarrow 2FeAsO_4 + 3H_2SO_4 \quad (11)$$

A flowsheet for bacterial leaching for treating sulfide ore/concentrate is shown in figure 6 [44].

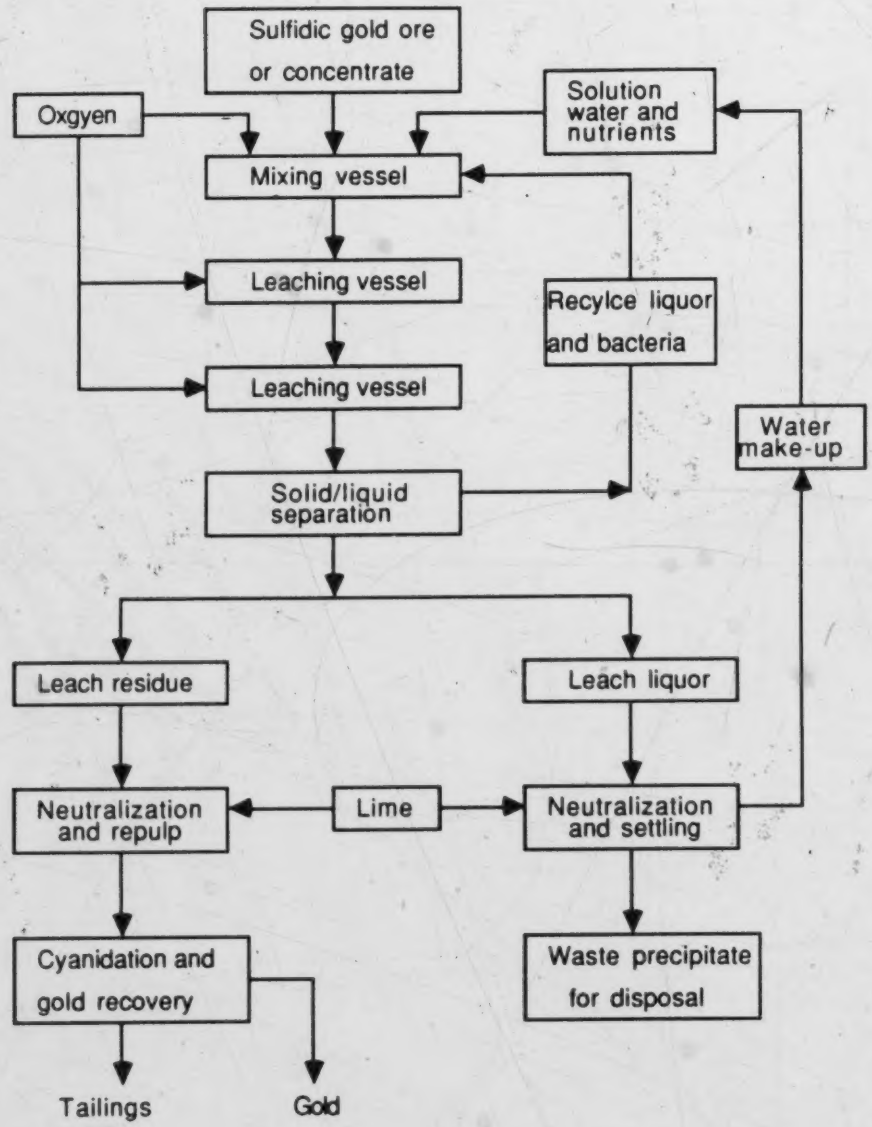

Figure 6. Bacterial treatment of gold-bearing sulfide ore/concentrate.

2.2.4 CHLORINATION PRETREATMENT

The adverse effects of carbonaceous material in the cyanidation of gold ores have been known for many years. In some gold mines, mining had to be suspended altogether in areas containing too much carbonaceous ore [4]. Carbonaceous ore that contain preg-robbing carbon are normally rendered "non-preg robbing" after efficient chlorination treatment. However, such ores still contain significant amounts of organic carbon, commonly in amounts comparable to the original amounts present prior to chlorination. It has been a common misconception that forms of organic carbon and sulfide sulfur are simply oxidized and removed almost entirely from carbonaceous ores during chlorination. This is certainly not the case for organic carbon, and only partially valid for sulfur in the form of sulfide minerals [100].

Chlorination studies on coal macerals had shown that, the organic complexes of exinite and fusinite are broken down to form chloro-derivatives of complex aromatic compounds. HCl is a major reaction product, and there is some loss of carbon as CH_4 and C_2H_6 with an increase in chlorination. Such compounds as dichlorodiphenyl, phenylmethyl chloride, and 2:6-dichloronaphthalene were identified by gas chromatography, ultraviolet spectrometry, infrared spectrometry, and elemental analysis [101].

It has also been suggested that the organic carbon probably undergoes chlorine reaction and fixation, resulting in "non-preg robbing" forms of chloro-derivatives that remain in the ore as essentially inert phases during subsequent cyanidation [100]. The use of chlorine to pretreat carbonaceous gold ores has been successfully employed at Carlin and Jerritt Canyon Mines for several years [24, 66], but due to the increased complexity of the ore and the increased cost of chlorine, investigations into the metallurgy of gold extraction from carbonaceous ore have again been initiated [37]. The U.S Bureau of Mines also developed a technique for generating in-situ hypochlorite ion in an ore pulp. The technique, known as electrooxidation, consist of adding sodium chloride to the ore pulp,

placing electrodes in the pulp, and passing an electrical current [102]. Recent developments of the chlorination process now eliminates the pre-oxidation stage and applies a straight forward wet chlorination only. Depending on the activity of the carbonaceous materials, extremely high chlorine consumption rates are experienced. This has forced the introduction of a new process "flash chlorination". The flash chlorination basically makes use of a different design of leaching vessels which offer high efficiency in chlorine gas dispersion and over all utilization [71].

CHEMISTRY OF CHLORINATION PROCESS

Rapid addition of chlorine gas (flash chlorination) causes the pH of the ore to drop to somewhere between 1 and 2.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl \qquad (1)$$

However the pH remained neutral on the slow addition of chlorine gas since the HCl formed reacts slowly with the calcareous gangue material to give calcium chloride.

$$2HCl + CaCO_3 \longrightarrow CaCl_2 + H_2CO_3 \qquad (2)$$

The active oxidizing species obtained on rapid addition of chlorine gas is principally HOCl. Slow addition of chlorine gas results in production of $Ca(OCl)_2$ as the principal oxidizing species.

$$2HOCl + CaCO_3 \longrightarrow Ca(OCl)_2 + H_2CO_3 \qquad (3)$$

The amount of chlorine gas escaping from the pulp can be excessive. To overcome this problem, sodium hydroxide or lime is added to the slurry before the addition of chlorine gas. The chlorine gas reacts with the base to form calcium or sodium hypochlorite.

$$Cl_2 + 2NaOH \text{ ----> } NaOCl + NaCl + H_2O \quad (4)$$

$$2Cl_2 + 2Ca(OH)_2 \text{ ----> } Ca(OCl)_2 + CaCl_2 + H_2O \quad (5)$$

The hypochlorite or oxidizing species then reacts with carbonaceous materials in the ore, passivating the activated-type carbon and breaking down the hydrocarbon chains and humic acid-type components [20]. It also converts the metal sulfides to chlorides which can hydrolyze to hydroxides depending on the pH of the slurry [37]. The flowsheet of a conventional chlorination process for pretreatment of carbonaceous ores and concentrates is shown in figure 7 [38].

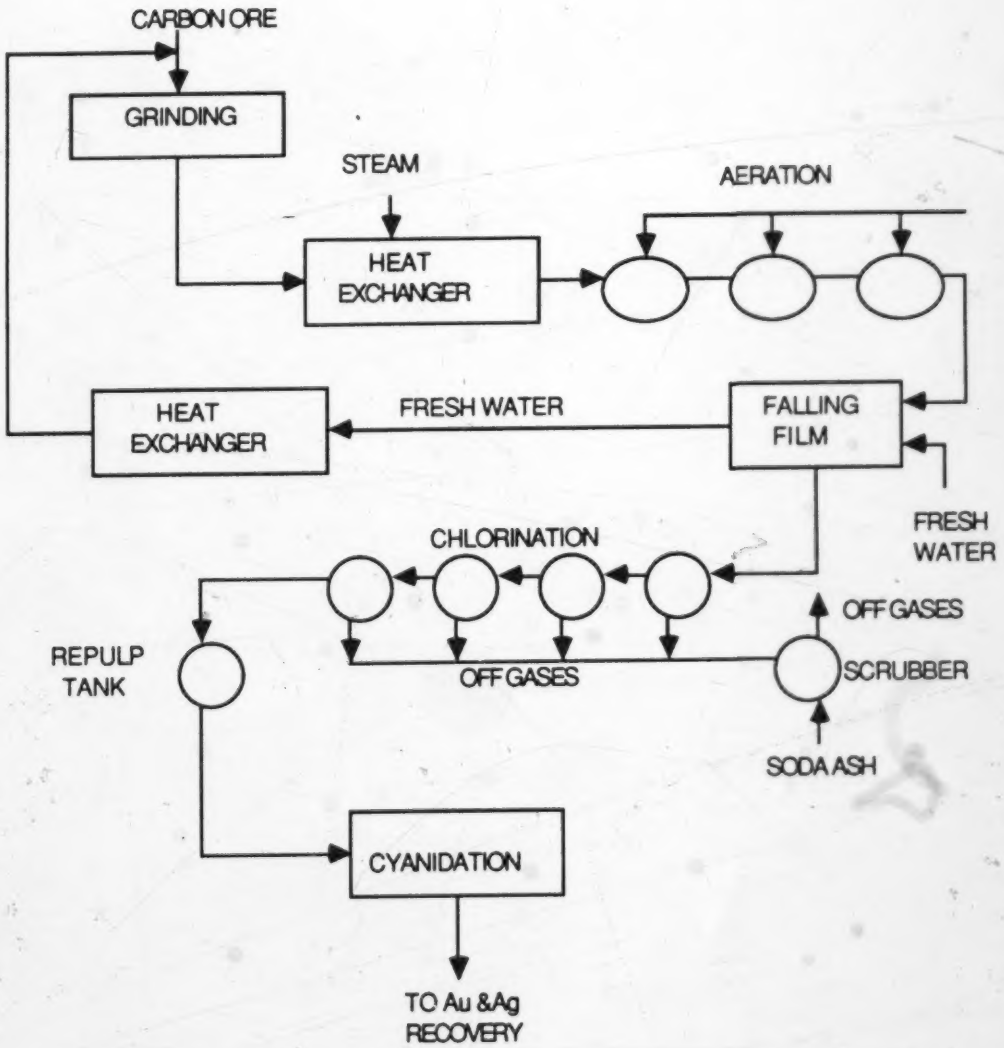

FIGURE 7. Conventional chlorination flowsheet for pretreatment of carbonaceous ores/concentrates.

2.2.5 CARBON/RESIN-IN-PULP AND IN-LEACH PROCESSES

Although gold forms a large number of complexes with various ligands, e.g. thiourea (gold I), thiocyanate (gold I), cyanide (gold I), chloride (gold III) and thiosulfate (gold I), among others, the interaction between activated carbon and the chloride and cyanide complexes of gold have received almost exclusive attention in the literature [103], probably because of their significance in the hydrometallurgical recovery of gold.

Activated carbon is used to recover gold from solution under two conditions, each of which demands significantly different process designs. One is the application in which the solution is an integral part of an ore slurry and in the other nominally clear solutions are treated [104]. The carbon-in-pulp process recovers gold in solution from slurry streams by contacting the carbon with the pulp and separating the two by screening. The leach and adsorption circuits are occasionally combined and are then described as the carbon-in-leach process. This carbon-in-leach system has advantages where carbon enhances the leach efficiency by removing surface coatings or competing with other gold-adsorbing constituents in the ore or concentrate [104]. In the resin-in-pulp process, resins are used for the adsorption of gold cyanide complex. Carbon-in-leach has been used to improve gold recovery from a flotation concentrate containing 0.9 to 1.9% carbon [105]. Strong-base resins have also been used successfully in some cases of high concentrations of organic compounds [106], since resins are known to be far less susceptible to organic and inorganic fouling than activated carbon [107], and also have fast kinetics and high loading capacity [106]. Carbon 'fouling' has been recognized as a major problem in many carbon-in-pulp plants [108, 109]. Poor adsorption characteristics of activated carbon in carbon-in-pulp plants have been attributed to high concentration of natural organic compounds (humates and fulvates) [106] and clay-type minerals [110] in ores. Humates and fulvates are known to be adsorbed readily on to activated carbon, and to adversely affect its adsorption properties for gold cyanide complexes [111].

Ion exchange resins are now said to be an attractive alternative to activated carbon in both column and in-pulp processes for the recovery of gold from cyanide solution. Resins are widely used for this purpose in the Soviet Union apparently in preference to activated carbons [112, 113]. The anionic gold complex, $Au(CN)_2^-$, is selectively adsorbed onto weak and strong base resins. However, other anionic cyanide complexes, cyanide ions and other anions from the process water are also adsorbed onto resin sites [112]. Resins are claimed to have more favorable equilibrium loading of gold than carbon and easier elution from the gold loaded resin than from gold loaded carbon [107]. Although only pilot resin-in-pulp gold recovery plants have been run, both resin-in-column and resin-in-pulp techniques are widely used in the large scale extraction of the anion complexes of uranium [113, 114].

The U. S. Bureau of Mines has also investigated the recovery of gold by chlorination of refractory carbonaceous and sulfidic ores, in which a ground ore pulp is contacted with chlorine gas and activated carbon is added to the pulp for a carbon-in-chlorine leach (CICL). Results showed that the organic carbon deactivating environment lowers, but does not eliminate the adsorption of gold on activated carbon [115]. Although some work has described the carbon adsorption of gold from aqueous chloride solutions [116, 117], chlorination circuits are designed primarily to deactivate organic carbon as a pretreatment, and the CICL scheme has not been pursued in industry [118, 119]. It is claimed that the hypochlorite ion assumed to be the deactivating agent [20] in chlorination circuits does not totally deactivate activated carbon at conventional carbon-in-pulp and carbon-in-leach carbon-to-solution ratios and hypochlorite concentrations [115]. Continual chlorine sparging was necessary to keep the organic carbon deactivated. Without activated carbon in the chlorine leach, the gold is readsorbed by the organic carbon as it reactivates in the decreasing presence of hypochlorite ion [115].

CARBON ADSORPTION MECHANISM

The mechanism by which activated carbon adsorbs gold cyanide, $Au(CN)_2^-$, has been a subject of research interest since 1913. Despite the commercial importance of the process no consensus has been reached as yet regarding the exact mechanism by which $Au(CN)_2^-$ (as well as $Ag(CN)_2^-$ and other base metal cyanide complexes) is adsorbed onto activated carbon [120]. Earlier workers postulated a reduction mechanism for the adsorption of aurocyanide on carbon [59, 121, 122]. The reducing agent was assumed to be carbon monoxide occluded by the carbon. Initially the adsorption of an addition compound of the type AuCN, CO or $(CN)_2$ on the carbon was proposed [59]. Later, the hypothesis that gold cyanide was adsorbed on carbon without chemical change as $NaAu(CN)_2$ was advanced [123]. This mechanism was generally accepted until it was found that the sodium content of carbon loaded with $NaAu(CN)_2$ and then burnt was not sufficient to account for the amount of gold present [124]. The following mechanism for the adsorption of gold on activated carbon was subsequently suggested [125].

$$2Na[Au(CN)_2] + Ca(OH)_2 + CO_2 \longrightarrow Ca[Au(CN)_2] + 2NaHCO_3 \qquad (1)$$

The improved loading at low pH values was attributed to the decomposition of the $Au(CN)_2^-$ and $Ag(CN)_2^-$ complex anions in the presence of acid, according to equations (2) and (3):

$$Au(CN)_2^- + H^+ \longrightarrow AuCN_{(s)} + HCN \qquad (2)$$

$$Ag(CN)_2^- + H^+ \longrightarrow AgCN_{(s)} + HCN \qquad (3)$$

It was thought that highly insoluble AuCN and AgCN were precipitated on the carbon [125]. An alternative mechanism to explain improved loading at low pH was the

electrostatic attraction of $Au(CN)_2^-$ anions to positively charged carbonium sites [126]. Later work showed that the presence of simple anions in the cyanide solution did not affect the capacity of carbon for gold cyanide and it was argued that the interactions between the $Au(CN)_2^-$ anion and the carbon were not electrostatic in nature [127]. It was proposed therefore, that under acidic conditions, the neutral molecule $HAu(CN)_2$ is concentrated on the surface of the carbon by a capillary condensation mechanism, whereas, under neutral or alkaline conditions, the $Au(CN)_2^-$ anion is retained on the carbon together with an equivalent amount of an alkali cation such as K^+ or Na^+ which is held on the carbon electrostatically. 'Dispersion forces' were suggested as being responsible for the retention of $HAu(CN)_2$ and $Au(CN_2^- Na^+)$ species on the carbon [127]. According to this theory the nature of the adsorbed form of gold cyanide is different in alkaline and acid solutions [127].

A study of the adsorption of gold cyanide on various activated carbons also indicated that gold adsorption is not a property of the carbon surface, since certain chemical treatments of the carbon (for example, with a mixture of nitric and hydrochloric acids at 80°C) prevent gold adsorption [104]. However, it was pointed out that a special type of micropore might be involved. Recently, a detailed investigation of the factors that affect the adsorption of silver cyanide on activated carbon was carried out [128]. Although these investigations concluded that the $Ag(CN)_2^-$ anion is adsorbed, they excluded an electrostatic interaction between the $Ag(CN)_2^-$ anions and positive sites on the carbon surface, at least for adsorption from alkaline solutions. Instead, an adsorption mechanism was advanced that is in accordance with an ionic solvation-energy theory [129] that accounts for the specific adsorption of anions on metal electrodes. According to this model, the degree and type of ionic hydration are the principal factors that determine specific adsorption. Applied to carbon, the theory predicts that a large, weakly hydrated anion such as $Ag(CN)_2^-$ will be specifically adsorbed on the carbon surface after losing some of its primary hydration water molecules, whereas some anions with large number of

strongly bound water molecules in their primary hydration shells, for example CN^-, will not be specifically adsorbed and will therefore remain in the outer part of the electrical double layer [128]. Figure 8 shows a flowsheet of a carbon-in-pulp plant for the recovery of gold and silver [120].

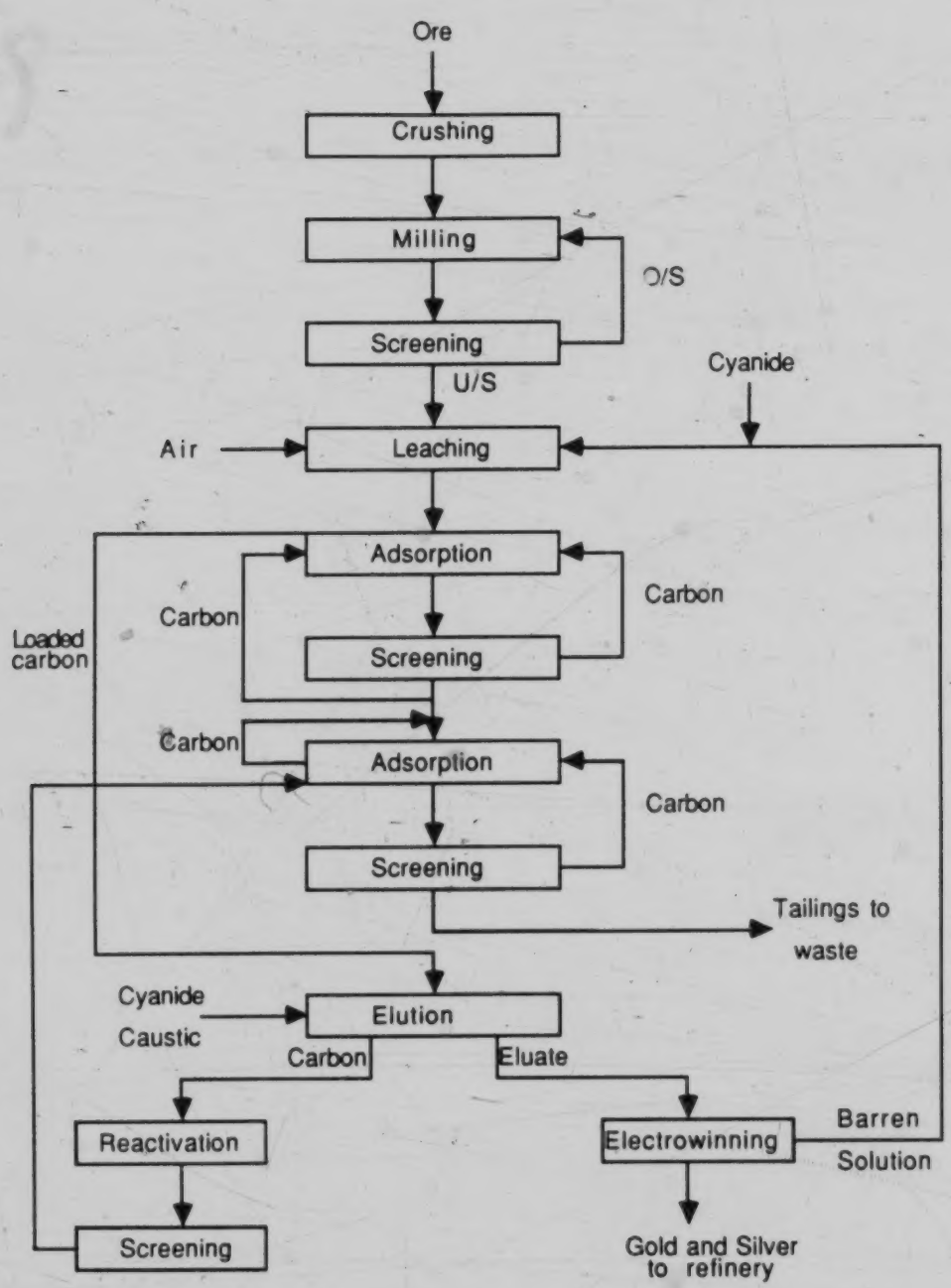

Figure 8. Flowsheet of a carbon-in-pulp plant for recovery of gold and silver

RESIN ADSORPTION MECHANISM

The most important difference between carbon-in-pulp and resin-in-pulp process is the chemistry of adsorption and elution of the resin [130]. The functional group of a strong-base resin is a quaternary amine possessing a permanent positive charge. Gold cyanide and other anions are therefore extracted by an ion-exchange reaction, which can be illustrated for aurocyanide by equation (1) :

$$\text{I-N}^{+}\text{R}_3\text{X}^{-} + \text{Au(CN)}_2^{-} \text{ ----> } \text{I-N}^{+}\text{R}_3\text{Au(CN)}_2^{-} + \text{X}^{-} \qquad (1)$$

where the symbol I- denotes the inert backbone or matrix of the resin, which is generally polystyrene. Other anions that occur commonly in cyanide leach liquors are $Ni(CN)_4^{2-}$, $Co(CN)_6^{3-}$, $Cu(CN)_4^{3-}$, $Zn(CN)_4^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, all of which are extracted by a strong-base resin, according to an ion-exchange reaction similar to that depicted in equation (1).

The complex metal cyanide on the resin can be eluted from the resin either by ion-exchange, in which the equilibrium depicted in equation (1) can be forced to the left-hand side by an increase in the concentration of X, or by conversion of the metal ions to non-anionic complex species. The latter technique involves the thiourea ligand, which , in the presence of strong mineral acids, forms a cation complex with gold, according to equation (2).

$$\text{I-N}^{+}\text{R}_3\text{Au(CN)}_2^{-} + 2(\text{NH}_2)_2\text{CS} + 2\text{H}_2\text{SO}_4 \text{ ----> }$$
$$\text{I-N}^{+}\text{R}_3\text{HSO}_4^{-} + [\text{Au}\{(\text{NH}_2)_2\text{CS}\}_2]^{+}\text{HSO}_4^{-} + 2\text{HCN} \qquad (2)$$

In the ion-exchange elution technique, anions such as chloride, bisulfate, nitrate, thiocyanate, or cyanide are used to reverse the ion-exchange equilibrium shown in equation (1).

Weak-base resins contain primary, secondary, or tertiary amine functional groups (or a mixture of these) and the ion-exchange properties of weak-base resins are governed by the pH value of the solution in contact with the resin. The greatest advantage of weak-base over strong-base resins is that they can be eluted by simple acid-base hydrolysis. The adsorption and elution of gold cyanide from a weak-base resin by hydrolysis is illustrated by equations (3) and (4) respectively.

$$\text{I-N}^{+}\text{R}_2\text{HX}^{-} + \text{Au(CN)}_2^{-} \dashrightarrow \text{I-N}^{+}\text{R}_2\text{HAu(CN)}_2^{-} + \text{X}^{-} \qquad (3)$$

$$\text{I-N}^{+}\text{R}_2\text{HAu(CN)}_2^{-} + \text{OH}^{-} \dashrightarrow \text{I-NR}_2 + \text{Au(CN)}_2^{-} + \text{H}_2\text{O} \qquad (4)$$

Weak-base resins can also be eluted in acid solution by an ion-exchange reaction [130]. Figure 9 shows a continuous countercurrent resin-in-pulp flowsheet for gold adsorption [120].

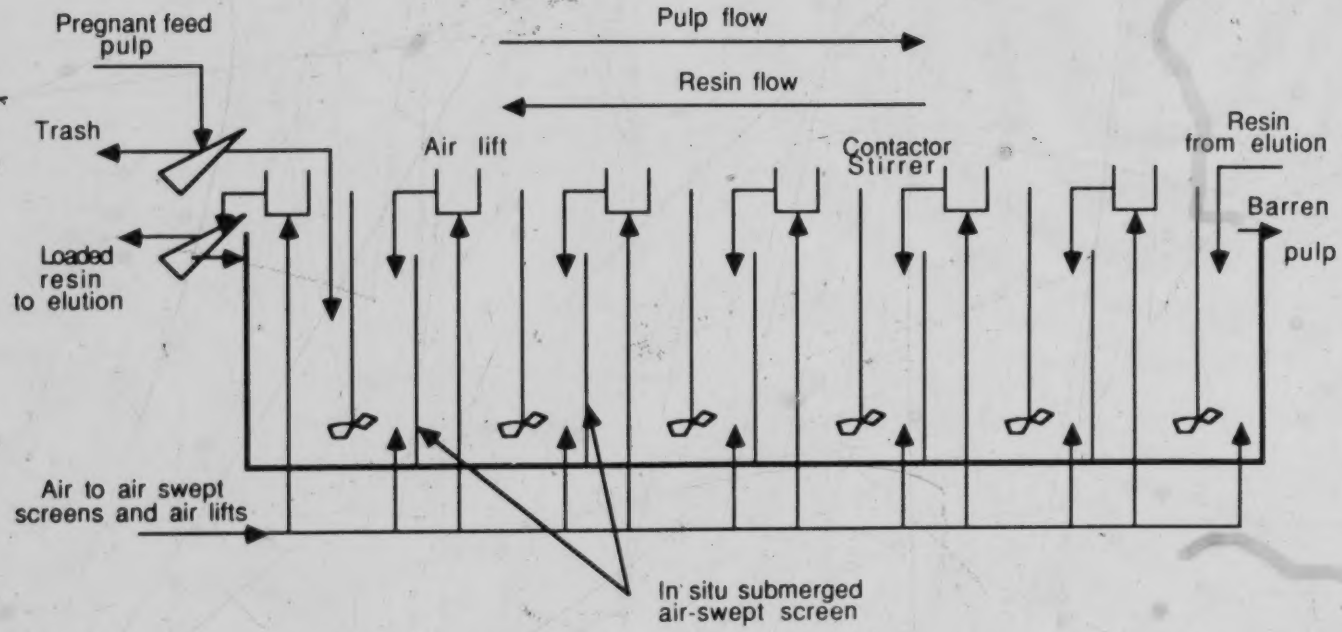

Figure 9. Continuous countercurrent resin-in-pulp flowsheet for gold adsorption.

2.2.6 ENVIRONMENTAL CONCERNS

Classical treatment of complex sulfidic ores such as the arseniferrous Campbell Red Lake and Giant Yellowknife deposits involves an oxidative roast of a flotation concentrate [131, 132]. Most of the papers presenting details of roasting practice propose theories regarding the effect of roasting temperature on the subsequent cyanidation of the calcine [132, 132] without considering its environmental effects. Despite its established practice roasting is not considered particularly attractive with today's standards for high product recovery and clean environment [2, 93]. The generation of sulfur, arsenic, antimony, and mercury-containing gases is most undesirable from an environmental standpoint [134] and control is extremely expensive, and therefore in recent years there has been a considerable interest in pressure hydrometallurgy as an alternative to roasting for liberating gold from sulfides [1].

Problems arise due to the need for SO_2 control and when arsenic is present, as it is in many cases, its efficient capture or stabilization as a waste can add considerably to the cost [134] and complexity of a gold roaster installation [77]. Because of the potentially harmful effects of sulfur dioxide (SO_2) on all aspects of the environment, i.e. health, vegetation and property, many countries, particularly the industrialized ones, have promulgated legislation to limit the amount of SO_2 that may be emitted to the atmosphere [135]. In many countries, air pollution control regulations have been developed covering ambient air quality standards (to protect public health and welfare) and emission standards (which limit the absolute quantity of pollutant which may be emitted to the atmosphere). Expensive devices such as electrostatic dust precipitators, baghouses, and high-efficiency scrubbers are necessary to meet the requirements [38].

In the past, many plants were often located in remote, arid regions where damage to the environment is perhaps less severe and more acceptable. The roasters were designed to meet the standards of the time when it was accepted practice to disperse gases into the atmosphere via a stack. There was therefore little incentive for sulfur and arsenic

containment. In cases where roaster and/or converter gases are converted to sulfuric acid, sulfur recovery varied from around 50 to 70% [135].

Arsenic with its tendency to form both volatile and stable compounds, can be eliminated in the processing of ores and concentrates by volatilization, or it can be retained in the final product, necessitating further processing or rendering the final product useless. Arsenic, with multiple valence states of -3, +3 and +5 combines with other elements to form over 245 mineral species. Some of these compounds are stable and others are volatile. The thermochemical behavior for most of these compounds is, however, unknown [136]. In practice the disposal of arsenic is normally accomplished by the formation of metal arsenates [137], calcium arsenate in particular. Calcium arsenate compounds are extremely insoluble in alkaline solution [138]. However, under the influence of carbon dioxide in the air, calcium arsenate decomposes to calcium carbonate and results in the leaching of arsenate into solution [139]. Sulfur and arsenic may also be recovered as sulfuric acid and arsenic trioxide respectively, both of which may be sold. Scrubbing of SO_2 with lime is also possible, but probably as expensive as neutralizing the sulfate solution produced in the wet oxidation processes [38].

To prevent environmental concerns related to SO_2 and As_2O_3, microwave irradiation has been studied on concentrates in the presence of NaOH, which was added in excess of the stoichiometric requirement for the formation of Na_2SO_4 and $NaAsO_4$ [74]. It was suggested that if roasting of refractory concentrates could be conducted in the absence of oxygen (i.e in vacuum or in an inert atmosphere), then the formation of these oxides could be avoided. In H_2SO_4 pressure oxidation, dissolved arsenate precipitates as scorodite ($FeAsO_4.2H_2O$) and reports to a jarosite-bearing leach residue [1, 28]. However, controversy also exists regarding scorodite's environmental stability [140, 141].

3. EXPERIMENTAL

3.1 MATERIALS

The double-refractory concentrate used was obtained from Ashanti Gold Field Corporation in Ghana. This concentrate is a desliming cyclone overflow of a sulfide flotation concentrate. The cycloning operation from which this sample was collected is intended to separate an initial flotation concentrate into a sulfide fraction, containing most of the gold, and a barren carbonaceous fraction. Due to the submicroscopic nature of the gold content and the intimate association of the sulfide minerals with carbonaceous materials, both the cyclone overflow and underflow contain appreciable amounts of sulfide minerals and carbonaceous materials. The overflow tends to be richer in carbonaceous materials but contain significant amounts of gold, which is currently not recovered. The concentrate is black in color indicating an intimate coating of carbonaceous materials on the surface of the other mineral particles.

Samples of the cyclone overflow slurry were collected over a period of two months, dried at 100°C, and 20kg of the dried concentrate was shipped for the study.

3.2 ANALYSIS

The bulk of the concentrate was riffled into smaller portions using Jones riffle samplers and splitters. Duplicate portions of 200g samples were used for wet sieve analysis to determine the size distributions of the concentrate. Samples of the 30g, 20g, and 10g portions were used for pressure oxidation and roasting runs, while a portion of the 30g samples was used for fire assay analysis. The 5g, 2g and 1g samples were used for aqua regia (HCl/HNO_3 acids) and hydrofluoric acid (HF) digestion of the concentrate and for the preparation of specimens for the X-ray and SEM analysis. The 1g samples were also used for chemical analysis of the concentrate.

3.2.1 SIZE ANALYSIS

Wet sieve analysis was done on the concentrate using the American Tyler series laboratory test sieves of sizes between 38 μm and 150 μm. Since the concentrate mainly consisted of very fine particles (< 38 μm), Lab-Tec (Model 100) particle size distribution analyzer was also used to determine size analysis of particles below 38 μm.

3.2.2 X-RAY DIFFRACTION ANALYSIS

Powder diffraction patterns of the concentrate and oxidation residues were obtained on a Philips PW 1380 Diffractometer equipped with a horizontal goniometer. The samples were scanned at 0.5°/min. from 4 to 30° using copper K-alpha radiation and a curved graphite monochromator filter.

The concentrate was also treated with hydrofluoric acid (HF) to remove quartz, whose major X-ray diffraction peak overlaps the main graphite (002) peak [69]. The HF treated residues were then analyzed by X-ray diffraction to determine the type of carbonaceous materials present in the concentrate.

Compounds were identified by either the Hanawalt search method [142] or by matching the pattern of the unknown with tabulated patterns. A match with a detailed pattern published in the ASTM Powder Diffraction file [143] was considered confirmation of the presence of a compound.

3.2.3 SCANNING ELECTRON MICROSCOPY ANALYSIS

Samples of the concentrate were prepared and viewed in an ISI-60 Scanning Electron Microscope (SEM) operated at 30 kev. The samples were prepared by placing 1g riffled samples on carbon stubs coated with colloidal graphite in isopropanal paste. The microscope is equipped with a Princeton Gamma-Tech (PGT) System 4 Energy Dispersive X-ray Analyzer (EDA) which gave a semi-quantitative elemental analysis of the

concentrate. With the EDA only elements of atomic number greater than 10 (neon) could be detected.

The EDA analysis gave an indication of the elements present and this was used to estimate the fluxes necessary for the fire assay determination of gold. In the scanning mode it gave an indication of the intimate association of sulfur, iron and arsenic with other materials in the concentrate. The SEM was also used to analyze gold beads obtained after crucible assay, cupellation and parting to ascertain that the beads were free from other metals (lead and silver) before weighing.

3.2.4 FIRE ASSAY

The gold content of the concentrate was determined by the conventional fire assay method. Based on the X-ray diffraction and SEM analysis, fluxes were chosen for the crucible assay [144]. Three different sets of charges were used:

	Charge 1	Charge 2	Charge 3
Concentrate	1 assay ton	1 assay ton	1 assay ton
Sodium carbonate	30.0g	30.0g	33.6g
Potassium nitrate	8.0g	-	-
Borax glass	10.7g	8.0g	7.0g
Litharge	60.0g	70.0g	100.0g
Flour	3.0g	6.0g	8.0g
Silica	7.0g	7.0g	-
Silver nitrate	-	-	0.1073g

where 1 assay ton = 29.166g

The fluxes and the concentrate were thoroughly mixed and transfered into a fire-clay crucible and covered with some borax glass by sprinkling to prevent dusting during

fusion of the charge. The crucible was heated in a furnace at 900°C to 1000°C for 45 minutes. During the fusion process a portion of the litharge (PbO) is reduced to metallic lead which becomes the "collector phase". The high density molten lead and precious metals sink to the bottom of the clay crucible. The resulting melt was poured into a conical shaped iron mould. When it had solidified, the lead button was separated from the slag, cleaned, and hammered into a cube to remove any adhering slag and to assist in handling with tongs during subsequent cupellation [145]. The lead buttons were placed in cupels and heated in a muffle furnace pre-heated to 900°C for 30 minutes. During the last 15 minutes of the cupellation, the furnace doors were opened to admit sufficient air to promote oxidation of the lead, while at the same time the temperature of the muffle was reduced to 800°C. The resulting silver-gold Doré beads were weighed and rolled into thin sheets. The sheets were then parted with hot 1:7 volume ratio of nitric acid (1.42 specific gravity) and water, and the resulting gold "annealed" over an open flame to yellow color, cooled, viewed under a microscope and weighed.

Since initial crucible fusion tests on the concentrate resulted in black fused materials, without appropriate lead buttons for cupellation, the concentrate was roasted at 750°C before subsequent fire assay tests were conducted. Also because of problems due to the size of the beads obtained and the loss of gold during cupellation [144], silver nitrate was added to some of the charges.

3.2.5 CHEMICAL ANALYSIS

The carbon content of the concentrate, pressure oxidation residues, and roaster discharges were analyzed using the ASTM (D3178-73) method. With this method, 0.2g of the sample was burnt at 900 to 1000°C in a combustion tube packed with water and carbon dioxide absorbents. The increase in weight of the CO_2 absorption bulb was then used to calculate the carbon content of the sample.

The sulfur contents were determined on a Leco total sulfur analyzer. Gold in cyanide leach solutions and aqua regia digested solutions were analyzed by Atomic Absorption Spectrophotometry (AAS).

Arsenic and iron content of the concentrate and Lime Agglomeration Roast (LAR) residues were determined by nitric acid and aqua regia digestion and the filtrate analyzed by AAS. Extreme care was applied during all arsenic analysis by AAS since this element exhibits high instability and low absorbance values. Thus over dilution was always avoided. The arsenic and iron content of the concentrate were double checked with the classical potassium iodate and potassium permanganate methods, respectively [146].

The hydrocarbons in the concentrate were extracted by treating the concentrate with toluene in a soxhlet extractor for 25 days. The weight loss of the sample after the extraction gave an indication of hydrocarbons present in the concentrate.

3.3 PRETREATMENT AND CYANIDATION

The untreated concentrate was leached with alkaline sodium cyanide to investigate the percentage of the gold amenable to cyanidation without pretreatment of the concentrate. Carbon-in-leach and resin-in-leach cyanidation processes were also used to extract gold from the untreated concentrate to investigate the possibility of increasing gold recovery over direct cyanidation.

Pressure oxidation pretreatment using sulfuric acid, nitric acid, and hydrogen peroxide were used to oxidize the concentrate prior to cyanidation and the results compared with those of roasting pretreatment at 750°C. Lime agglomeration roast pretreatments were finally performed on the concentrate.

3.3.1 DIRECT, CARBON-IN-LEACH AND RESIN-IN-LEACH CYANIDATION PROCESSES

For the direct, carbon-in-leach and resin-in-leach cyanidation of the concentrate, slurries of the concentrate were first prepared (10g or 20g of concentrate/100ml of water). The pH of the slurries were adjusted to 11 ± 0.5 with lime. For the in-leach cyanidation, either activated carbon (+600 μm) or Amberlite IRA-400 resin (+600 μm) was added immediately after sodium cyanide (NaCN) addition. During the direct cyanidation, no adsorbents were added after sodium cyanide addition. Amberlite IRA-400 resin was used because of its strong affinity for anionic complexes [23]. After leaching for a predetermined period of time, the slurry was first passed through a 355 μm sieve to collect the adsorbents and subsequently filtered on fine filter paper. The gold loadings on the activated carbon or resin were determined by burning off the adsorbents. The gold in solution was determined by the AAS.

3.3.2 PRESSURE OXIDATION PRETREATMENT AND CYANIDATION

The pressure oxidation tests were conducted in a stainless steel jacketed 300 ml Parr autoclave equipped with teflon internals, a magnetic stirrer, a temperature controller and a pressure gauge. The temperature was maintained within ±1.0°C of the desired value and 99.9% purity oxygen was supplied to the autoclave via a dip tube. The sample slurry was prepared by mixing known amounts of water (100ml or 200ml) and the concentrate (10g, 20g or 30g) in the autoclave, to a predetermined percent solids, and adding drops of reagent grade acid (H_2SO_4, HNO_3) or hydrogen peroxide (H_2O_2) until the desired pH was achieved. The autoclave was then sealed and heated to the chosen reaction temperature. Once the reaction temperature was reached, oxygen was introduced until the required pressure was obtained. Oxygen partial pressure was typically in the range of 1000-3000kpa.

After the specified reaction time, the reactor was cooled and the content filtered, washed with one liter of water, dried and weighed. The solids from the pressure oxidation were subsequently divided into various fractions, which were used for carbon and sulfur analysis, and alkaline cyanidation. All cyanidation runs were conducted at ambient temperature with 1.0g/liter NaCN solution and at a pH of 11 ± 0.5. Lime was used for pH adjustments and an overhead stirrer for agitation in an open glass reaction vessel.

3.4 PREG-ROBBING ACTIVITY AND LEACHING KINETICS

Preg-robbing activity tests were performed on the concentrate, the pressure oxidation residues, and the roaster discharge by contacting a known amount of samples with a standard gold solution, and measuring the gold content of aliquots at various time intervals. The standard gold solution was obtained from Fisher Scientific Limited, 25ml of the standard 1000ppm gold solution was diluted to 1000ml to obtain 25ppm. Typically, about 50ml of 25ppm standard gold solution was mixed with 3g of the sample, and 1ml of aliquots were withdrawn at specific time intervals for AAS analysis. These experiments gave an indication of how active the concentrate and residues from the various pretreatment methods are in terms of adsorbing gold cyanide complex from solution.

Leaching kinetics tests were also performed on the concentrate, the pressure oxidation residues, and the roaster discharge. Slurries of the concentrate and residues, typically of 10g concentrate and 100ml of water, were prepared, the pH adjusted to 11 ± 0.5 and sodium cyanide added. During the leaching, 1ml aliquots of the leach solutions were drawn at various time intervals and gold in these solutions determined by the AAS. The percentage gold leached into solution at the various times were then calculated.

3.5 LIME AGGLOMERATION ROAST PRETREATMENT AND CYANIDATION

For the Lime Agglomeration Roast (LAR) pretreatment, the concentrate was agglomerated with reagent grade calcium hydroxide prior to roasting. The concentrate was mixed with known amounts of hydrated lime to give Ca:S mole ratios ranging from 0.5 to 2.0. The mixture was fed into a wrist shaker (Spex® Mixer/Mill) and mixed until a homogeneous mixture was obtained (10 minutes). The mixture was subsequently roasted at temperatures between 500 and 800°C in a tube furnace for 40 minutes.

The sulfur dioxide emitted during roasting of the agglomerates were determined by using a modified ASTM (D3177-75) method. Typically, 0.2g of the agglomerate was placed in a tared ceramic "boat" and the boat was placed into a modified tube furnace preset at the desired temperature and roasted by passing a stream of 99.9% purity oxygen. During the roasting, the sulfur dioxide (SO_2) in the roaster gases was absorbed in a 5 vol. % H_2O_2 solution contained in a measuring cylinder and connected to the furnace by means of a Tygon tubing. The resulting sulfuric acid produced was titrated against standard sodium hydroxide (0.05 N) solution. The end point was determined using a mixture of methyl red and bromcresol green indicator and double checked by using a pH meter to compare the starting and ending pHs. The percent sulfur emitted by the sample was calculated from the equation:

$$\%S = \frac{1.603 \text{ X } 0.05 \text{ X Volume of NaOH (ml)}}{\text{Weight of sample (g)}}$$

The sulfur dioxide "captured" during roasting was expressed as a percentage of the total sulfur dioxide emitted without addition of lime (i.e. Ca:S ratio = 0.0) at the same temperature.

The arsenic emitted was calculated based on the difference between the initial and final arsenic content of the agglomerates. The arsenic trioxide "captured" was also

expressed as a percentage of the total arsenic trioxide emitted without addition of lime at the same temperature.

After the sulfur dioxide and arsenic trioxide capture experiments, samples were generated at the various temperatures and Ca:S mole ratios in a muffle furnace. The generated samples were divided into various fractions, which were used for carbon analysis and duplicate alkaline cyanidation tests. Gold in cyanide leached solutions was analyzed with AAS.

4. RESULTS AND DISCUSSION

4.1 ANALYSIS

4.1.1 PARTICLE SIZE ANALYSIS

The particle size analysis of the concentrate using sieves and Lab-Tec (Model 100) Particle Size Analyzer are shown in Tables 1 and 2, respectively. From these tables it is observed that the concentrate is very fine. About 98% of the concentrate passed 38 μm (Table 1) and 32% passed 2 μm (Table 2). A Gaudin-Schuhmann plot of cumulative undersize data against sieve aperture (Table 2) on log-log graph gave a d_{50} and d_{80} of 3.5 and 7.5 μm respectively. These results are expected since the concentrate is a cyclone overflow of a sulfide flotation concentrate. From the literature, carbonaceous materials associated with gold are of very fine sizes [4, 53].

4.1.2 SCANNING ELECTRON MICROSCOPY

The SEM micrographs of pyrite and arsenopyrite particles (light images) associated with the untreated concentrate are shown in Plates 1 and 2 at magnifications of 700 and 3400, respectively. Though the gold is supposed to be associated with the sulfides (pyrite and arsenopyrite) and the SEM electron beam reveals morphological features at the surface and penetrates to a depth of about 5×10^{-3} μm, no gold particles were seen at these magnifications. Information presented by many workers on the nature of gold in carbonaceous ores indicates that gold is present as finely disseminated microscopic to submicroscopic grains and not visible under a microscope [4, 53, 67]. Other workers have described this type of gold as "invisible" gold [2].

Plates 3, 4, and 5 show X-ray maps of sulfur, iron and arsenic particles, respectively, in the concentrate. It is observed that there is a high degree of dissemination of the sulfur, iron and arsenic with the other materals in the concentrate. An SEM micrograph of a gold bead after parting with nitric acid is shown in Plate 6. After parting, the gold bead is

TABLE 1

PARTICLE SIZE ANALYSIS
OF CONCENTRATE USING SIEVES

SIEVE SIZE RANGE (µm)	WEIGHT (g)	% WEIGHT.	CUM. % UNDERSIZE	CUM. % OVERSIZE
+ 150	0.06	0.03	99.97	0.03
- 150 + 106	0.10	0.05	99.92	0.08
- 106 + 75	0.14	0.07	99.85	0.15
- 75 + 53	0.94	0.47	99.38	0.62
- 53 + 45	1.52	0.76	98.62	1.38
-45 + 38	1.04	0.52	98.10	1.90
- 38	196.20	98.10	-	-

TABLE 2

PARTICLE SIZE ANALYSIS OF CONCENTRATE
USING LAB-TEC (MODEL 100) PARTICLE SIZE ANALYZER

APERTURE SIZE (μm)	% WEIGHT.	CUM. % UNDERSIZE	CUM. % OVERSIZE
75	0.0	100.0	0.0
38	1.0	99.0	1.0
19	3.0	96.0	4.0
9	8.0	88.0	12.0
5	24.0	64.0	36.0
2	32.0	32.0	68.0
1	22.0	10.0	90.0
- 1	10.0	-	-

PLATE 1. SEM MICROGRAPH OF PYRITE PARTICLES
(X700), RIGHT HAND MARKER = 10 μm

PLATE 2. SEM MICROGRAPH OF ARSENOPYRITE PARTICLES
(X3400), RIGHT HAND MARKER = 1 μm

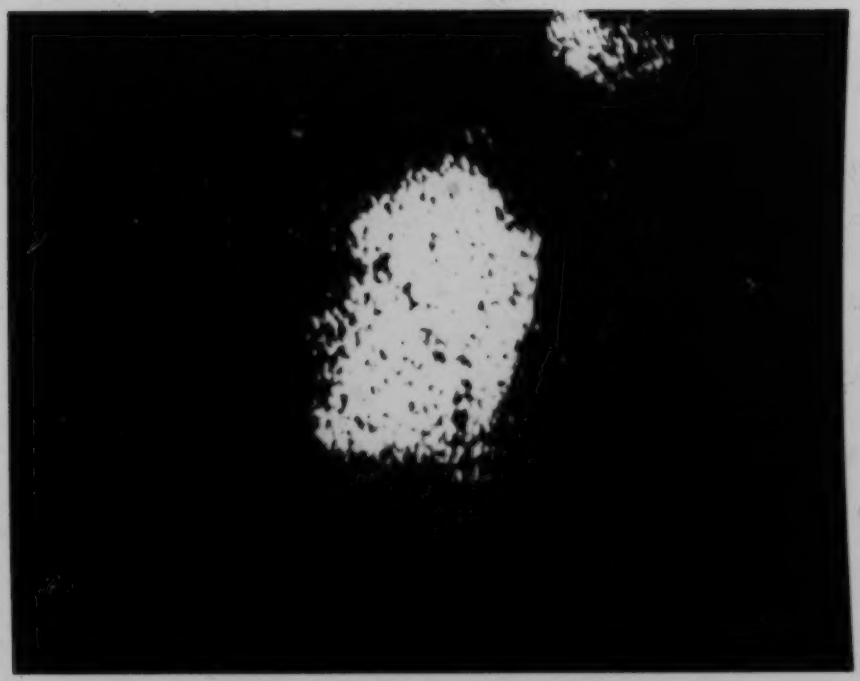

PLATE 3. X-RAY MAP OF SULFUR PARTICLES

PLATE 4. X-RAY MAP OF IRON PARTICLES

PLATE 5. X-RAY MAP OF ARSENIC PARTICLES

PLATE 6. SEM MICROGRAPH OF GOLD BEAD AFTER PARTING (X110), RIGHT HAND MARKER = 10 μm

viewed under the SEM to ensure that it is not contaminated with other metals. The parted gold is then "annealed" to make it more compact before weighing [144].

4.1.3 X-RAY DIFFRACTION

The powder diffraction patterns obtained for the untreated concentrate showed peaks characteristic of the following minerals:

Quartz (SiO_2)

Muscovite ($KAl_2(AlSi_3)O_{10}(OH)_2$)

Dolomite ($MgCO_3.CaCO_3$)

Ankerite ($Ca(Mg,Fe)(CO_3)_2$)

Chlorite ($(MgFe)_5Al(AlSi_3)O_{10}(OH)_8$)

Plagioclase ($(Na,Ca)Al(Si,Al)Si_2O_8$

Albite ($NaAlSi_3O_8$)

Most of these minerals were detected by other investigators who worked with carbonaceous ores from the same region [49, 53]. Sulfide minerals (pyrite and arsenopyrite) were not detected since only minerals with greater than 5% could normally be detected by the X-ray diffraction. The X-ray diffraction pattern of the hydrofluoric acid treated residue showed characteristic graphite peaks. This is an indication that a significant amount of the carbonaceous material in the concentrate is graphitic. The X-ray diffraction data of the residue is shown below :

d (A)	Intensity (%)	h k l
3.36	100	0 0 2
2.13	10	1 0 0
2.03	50	1 0 1
1.678	80	0 0 4
1.544	10	1 0 3

4.1.4 FIRE ASSAY AND CHEMICAL ANALYSIS

The gold beads obtained from the three different sets of charges used for the fire assay gave comparable results, although beads obtained from charges without silver nitrate were difficult to handle because of their extremely small sizes. Some of the beads obtained from charge 1 were contaminated with lead and were discarded.

Table 3 presents the elemental composition of the double-refractory concentrate. The data show a significant content of gold, carbon, sulfur, arsenic, and iron in this sample. The high content of sulfur and arsenic suggest that direct roasting of this concentrate as a pretreatment step will be undesirable due to the possibility of serious environmental problems.

The amount of hydrocarbon extracted from 50g of the concentrate using toluene was 0.11g (i.e. 0.22%). Radtke and Scheiner's analyses of the Carlin ore [70], yielded 0.012g (0.012%) of hydrocarbon from 100g of the ore, Afenya's analysis of Prestea, (Ghana) carbonaceous ore [49] yielded 0.067%, while Osseo-Asare obtained 1.07g from 400g (0.27%) using the same ore [53].

4.2 CARBON-IN-LEACH AND RESIN-IN-LEACH CYANIDATION

Table 4 shows the gold extraction data obtained from direct cyanidation, carbon-in-leach, and resin-in-leach cyanidation studies on the untreated concentrate. It is clear from Table 4 that a substantial portion of the gold cannot be extracted due to the refractory nature of the concentrate.

By definition, a concentrate is regarded as refractory when less than 80% of the gold content is extractable by direct cyanidation. At a low % solids of 10, only 53% of the gold could be extracted from this concentrate, while 49% is extracted at 20% solids.

TABLE 3

CHEMICAL COMPOSITION OF THE CONCENTRATE

ELEMENT	COMPOSITION
Au	32.57 g/tonne
C	9.37 %
S	3.53 %
As	1.29 %
Fe	7.36 %
Si	25.82 %
Ca	1.79 %
Mg	0.99 %
Al	10.25 %
K	2.28 %

TABLE 4

DIRECT CYANIDATION, CARBON-IN-LEACH AND
RESIN-IN-LEACH EXTRACTION DATA FOR UNTREATED CONCENTRATE

EXTRACTION PROCESS	% SOLIDS	ADSORBENT (kg/tonne)	% Au EXTRACTION
Direct Cyanidation	10	-	52.9
	20	-	49.0
Carbon-in-Leach	10	100	52.1
	10	200	53.7
Resin-in-Leach	10	100	42.8
	10	200	41.5

The addition of carbon and resin during the Carbon-in-Leach and Resin-in-Leach cyanidation processes did not improve the gold extraction. These adsorbents were added to the leach solution to improve extraction based on the premise that the gold will be adsorbed from solution at a faster rate by the adsorbents than by the carbonaceous materials present in the concentrate. Since their addition did not improve gold extraction, it appears that most of the gold is locked-up in the sulfides and carbonaceous materials and is not accessible by the cyanide solution. The refractoriness of this concentrate is therefore not only due to preg-robbing activity by the carbonaceous materials in the concentrate but also by the occlusion of fine gold particles by sulfides and carbon. Hence the concentrate is regarded as being double-refractory. The lower gold extraction observed with increase in resin from 100 to 200 kg/tonne during the Resin-in-Leach cyanidation is due to attrition of the loaded resin which is lost to the cyanidation tailings.

4.3 PRESSURE OXIDATION

The sulfuric acid pressure oxidation tests were performed under different experimental conditions including pressure, temperature, time, pH and slurry density. The effect of total oxygen pressure on sulfide and carbon oxidation, and gold extraction during sulfuric acid pressure oxidation at 130°C, 180°C, 200°C, and pH of 2.5 is illustrated in Figures 10-12. At 130°C (Figure 10), the sulfide oxidation increased from less than 3% at 1000 kpa to only about 10% at 3000 kpa. There was barely any increase in carbon oxidation with increase in pressure. Increase in gold extraction was also minimal. When the temperature was increased to 180°C under the same conditions (Figure 11), there was an increase in sulfide oxidation from less than 5% at 1000 kpa to only about 20% at 3000 kpa. Increases in carbon oxidation and gold extraction were again generally minimal. An increase in the temperature from 180°C (Figure 11) to 200°C (Figure 12) did not bring

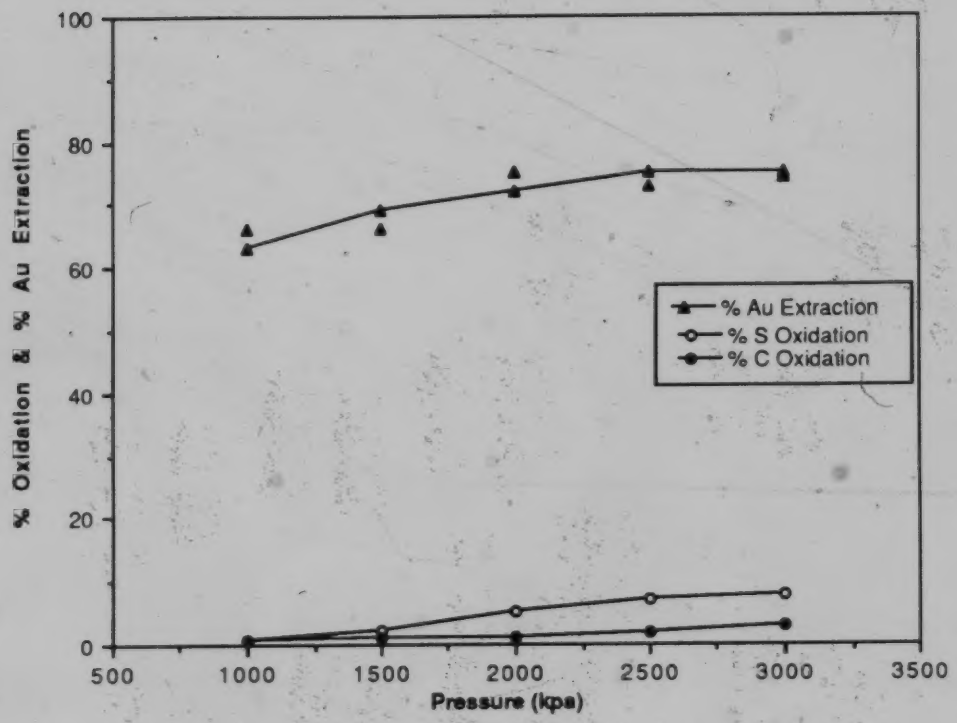

Figure 10. The effect of pressure on sulfide oxidation, carbon oxidation and gold extraction using H_2SO_4. (130°C; 30% solids; pH of 2.5; 1 hr autoclave time; 28 hrs cyanidation at 10% solids)

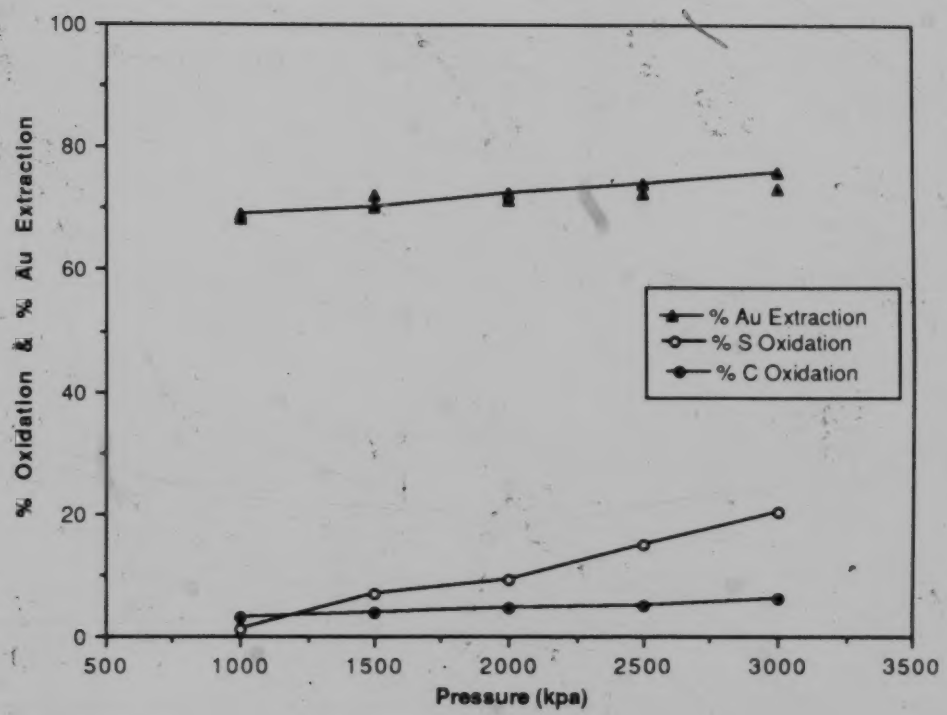

Figure 11. The effect of pressure on sulfide oxidation, carbon oxidation and gold extraction using H_2SO_4. (180°C; 30% solids; pH of 2.5; 1 hr autoclave time; 28 hrs cyanidation at 10% solids)

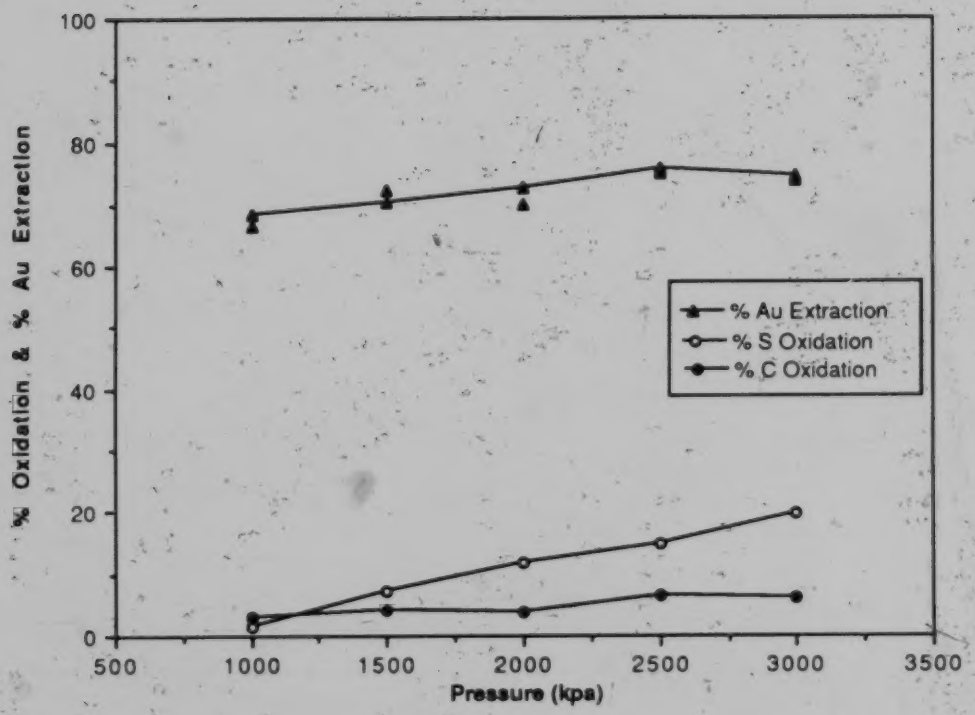

Figure 12. The effect of pressure on sulfide oxidation, carbon oxidation and gold extraction using H_2SO_4. (200°C; 30% solids; pH of 2.5; 1 hr autoclave time; 28 hrs cyanidation at 10% solids)

about any appreciable change in sulfide oxidation, carbon oxidation and gold extraction from those observed at 180°C. However, although carbon and sulfide oxidation was less than 5% at 1000 kpa (Figures 10-12), gold extraction increased from 53% for the untreated concentrate, to 68% for sulfuric acid pressure oxidation at 1000 kpa. This is an indication that even minimal oxidation of carbon and sulfide result in a significant increase in gold extraction probably due to physical liberation of some of the gold particles.

Figure 13 presents the effects of % solids on sulfide and carbon oxidation during sulfuric acid pressure oxidation at 200°C, and subsequent gold extraction. The degree of sulfide oxidation decreased slightly with increasing % solids, but the carbon oxidation and gold extraction remain virtually constant with increase in % solids.

Figure 14 shows the effect of temperature on carbon oxidation, sulfide oxidation and gold extraction for H_2SO_4 pressure oxidation. A more acidic pH of 1.5 was used in this case as opposed to 2.5 used for Figures 10-13. At this pH, the degree of sulfide oxidation increases sharply from about 12% at 130°C to over 90% at 180°C and 200°C. This results shows that the reaction pH is a very important parameter for the pressure oxidation of this concentrate. The data of Figure 14 also indicate slight increases in carbon oxidation and gold extraction with increase in pretreatment temperature. Based on the results in Figure 14, experiments were conducted to study the efffect of pH on oxidation efficiency and gold extraction, as shown in Figure 15. It is clear from Figure 15 that significant increases in sulfide oxidation occur with a decrease in pH. Less significant increases are observed in carbon oxidation with decreasing pH but tthe total amount of gold extraction remains relatively constant. Although sulfide oxidations above 90% are obtained at pH below 2.0, the gold extraction remained at the 65-70% range. This suggests that the residual carbon in the pressure oxidation residue is responsible for the low gold extraction even after complete sulfide oxidation.

Since all the autoclave oxidation experiments were conducted for 1 hour duration without appreciable carbon oxidation, the autoclave time was varied and its effect observed.

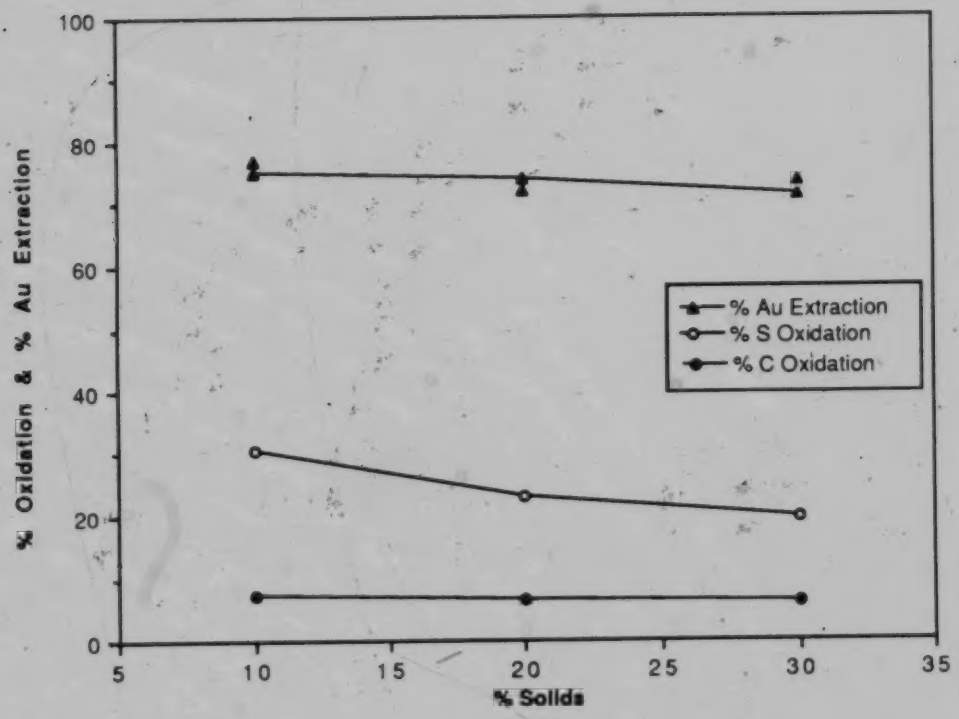

Figure 13. The effect of % solids on sulfide oxidation, carbon oxidation and gold extraction using H_2SO_4. (200°C; pH of 2.5; 1 hr autoclave time; 3000 kpa O_2; 28 hrs cyanidation at 10% solids)

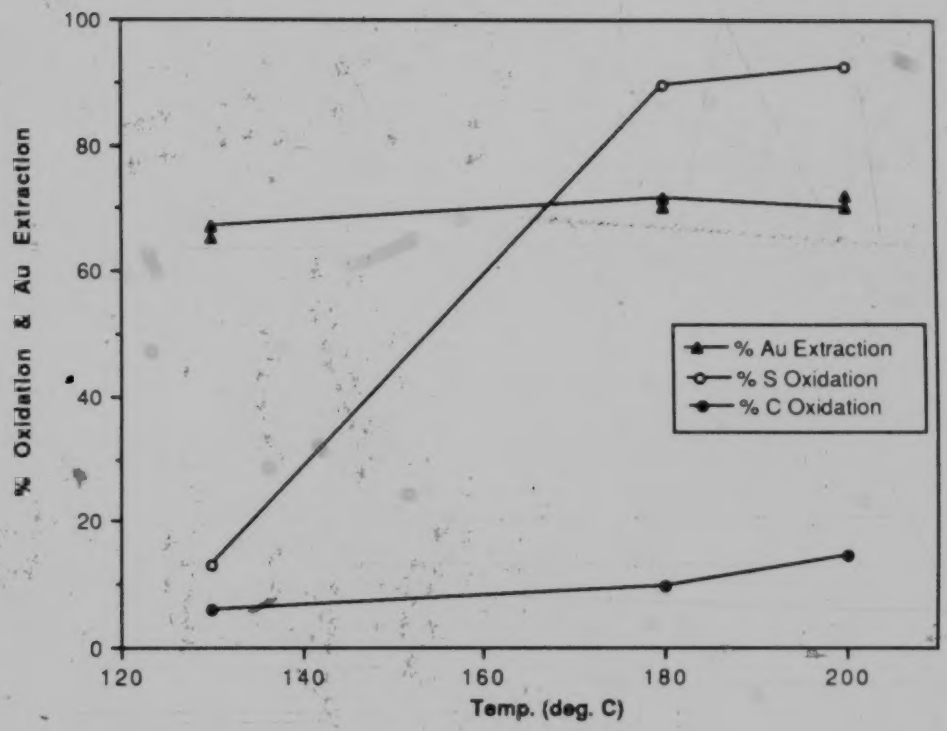

Figure 14. The effect of temperature on sulfide oxidation, carbon oxidation and gold extraction using H_2SO_4. (pH of 1.5; 1 hr autoclave time; 3000 kpa O_2; 10% solids; 28 hrs cyanidation at 10% solids)

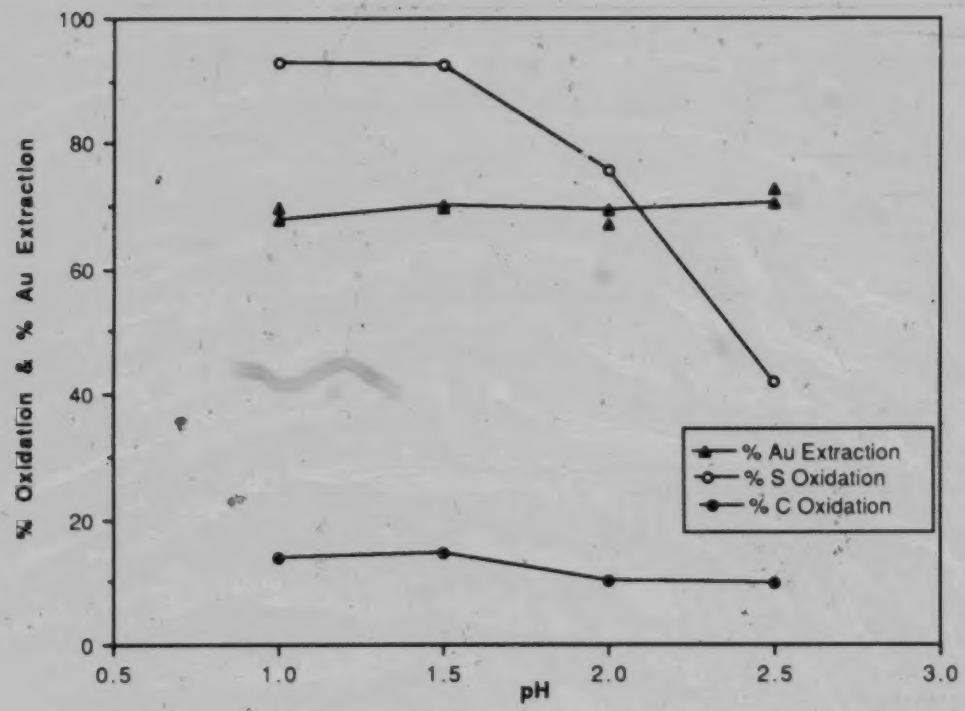

Figure 15. The effect of initial pH on sulfide oxidation, carbon oxidation and gold extraction using H_2SO_4. (1 hr autoclave time; 3000 kpa O_2; 10% solids; 200°C; 28 hrs cyanidation at 10% solids)

Figure 16 shows the effect of autoclave time on sulfide oxidation, carbon oxidation and gold extraction. There is no significant improvement in carbon oxidation beyond ½ hour. Sulfide oxidation increased steadily between 30 minutes and 2 hours, while a slight decrease in gold extraction is observed.

The results presented above indicate that sulfuric acid pressure oxidation does not oxidize most of the carbon content in this double-refractory concentrate. In addition, the carbonaceous materials seem to contribute more to the refractoriness of the concentrate than the sulfide mineralization. The limited level of carbon oxidation during H_2SO_4 pretreatment is an indication that the carbonaceous material in the concentrate is mostly graphitic. This is in agreement with the X-ray diffraction data of the HF treated residue which showed characteristic graphite peaks.

Figure 17 presents the results for sulfide oxidation, carbon oxidation, and gold extraction after pressure oxidation with nitric acid at 200°C, 10% solids, 3000 kpa, at pH of 1.5. The data show that sulfide oxidation above 95% is obtained after two hours, but only a slight increase is again observed for carbon oxidation. The level of carbon oxidation is similar to that observed with H_2SO_4 pretreatment. Similarly, only a marginal increase in gold extraction is indicated with time. Although the oxidation of sulfide is almost complete, the level of gold extraction is similar to those observed for the sulfuric acid pretreatment (65-70% range). The slight increase in carbon oxidation during nitric acid pretreatment does not translate to higher gold extraction. These generally low levels of gold extraction, in spite of almost complete sulfide oxidation, support the suggestion that refractoriness due to the presence of carbon is predominant. Since the amount of gold recovery increased from 53% for the untreated concentrate to above 65% for the residues from the acid pressure oxidation treatments, it is inferred that some of the refractoriness is attributable to the occlusion of fine gold particles by sulfide minerals.

Figure 18 shows the effect of hydrogen peroxide pressure oxidation on sulfide oxidation, carbon oxidation and gold extraction as a function of pretreatment time. The

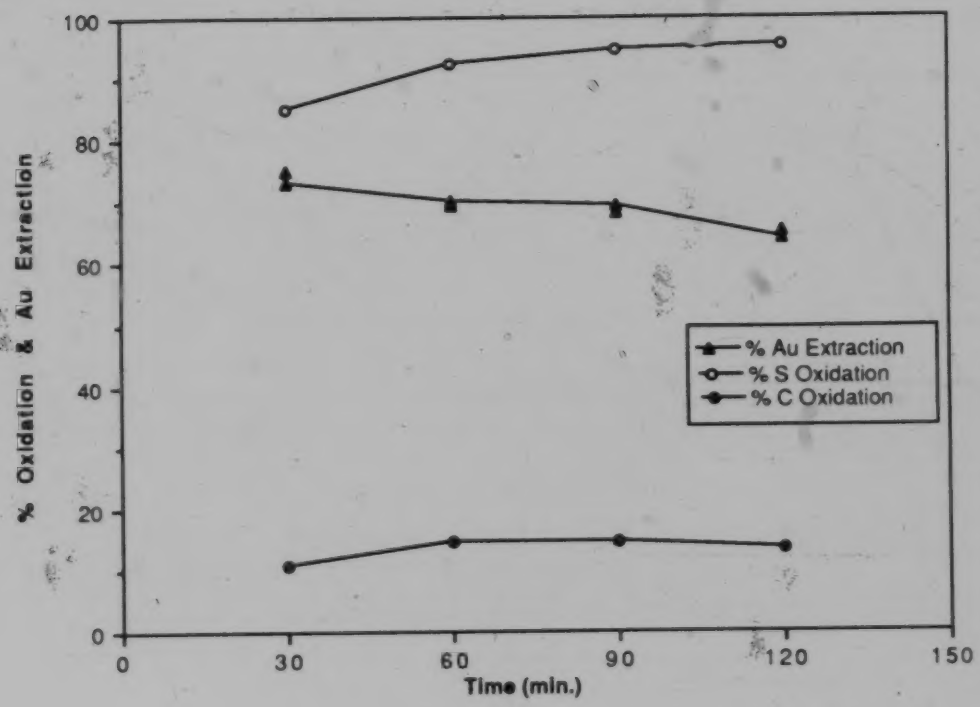

Figure 16. The effect of autoclave time on sulfide oxidation, carbon oxidation and gold extraction using H_2SO_4. (3000 kpa O_2; 10% solids; pH of 1.5; 200°C; 28 hrs cyanidation at 10% solids)

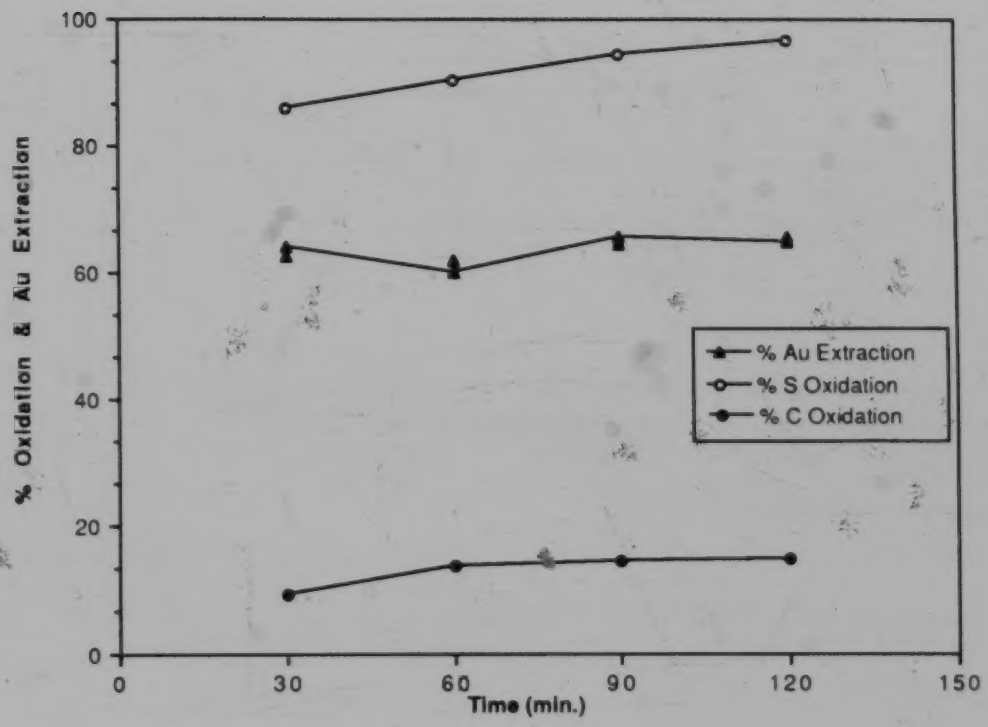

Figure 17. The effect of autoclave time on sulfide oxidation, carbon oxidation and gold extraction using HNO_3. (3000 kpa O_2; 10% solids; pH of 1.5; 200°C; 28 hrs cyanidation at 10% solids)

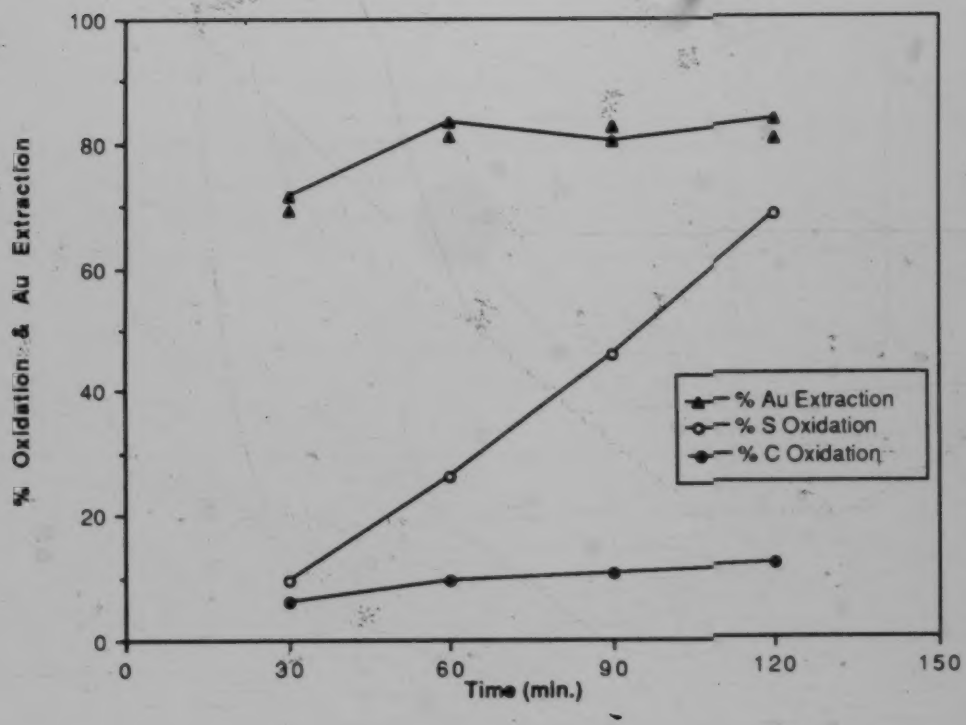

Figure 18. The effect of autoclave time on sulfide oxidation, carbon oxidation and gold extraction using H_2O_2. (3000 kpa O_2; 10% solids; pH of 6.5; 200°C; 28 hrs cyanidation at 10% solids)

level of sulfide oxidation after two hours of treatment is about 65%, and is lower than the levels for H_2SO_4 and HNO_3 pretreatments. The carbon oxidation levels are similar to those observed for the sulfuric acid and nitric acid oxidation. However, the level of gold extraction in the subsequent cyanidation increases to about 83% after peroxide pressure oxidation beyond one hour, as compared to the 65-70% range observed for the H_2SO_4 and HNO_3 pressure oxidation pretreatments. This higher gold extraction from the peroxide process, in spite of lower sulfur and carbon oxidation, suggests that the peroxide oxidation somehow inhibits or deactivates the preg-robbing activity of the carbonaceous materials in the concentrate. The mechanism for this deactivation is not clear at this time but deserves further investigation. The significant increase in gold extraction above 80%, despite insignificant carbon oxidation, is an indication that it is the preg-robbing activity, rather than gold occlusion, by the carbonaceous material that is partly responsible for the refractory nature of the concentrate.

Figure 19 presents comparisons between the results obtained for the three pressure oxidation methods used and the data obtained from roasting the concentrate at 750°C, in terms of maximum gold extraction, sulfide oxidation, and carbon oxidation. The figure shows that the highest gold extraction is obtained from the roasted samples due to the oxidation of most of the sulfide and almost complete removal of the carbonaceous materials. However, although sulfide and carbon oxidation for the acid pressure pretreatments were higher than those from peroxide oxidation, the peroxide pretreatment resulted in significantly higher gold extraction. Gold extraction of 83% was observed for the peroxide as compared to 65-70% for the acid pretreatments. The results show that apart from roasting, the peroxide pressure oxidation process may be adequate for the pretreatment of this concentrate before cyanidation. Pretreatment with the peroxide somehow reduces the preg-robbing activity of the carbonaceous materials leading to higher gold extraction.

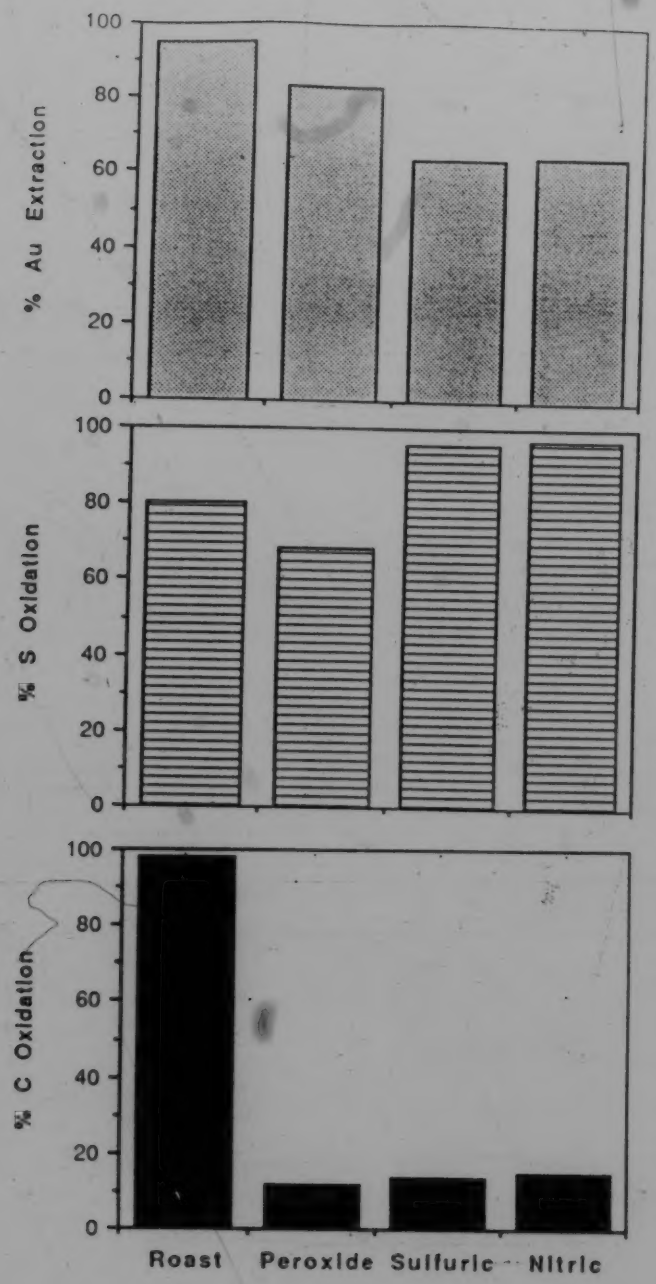

Figure 19. The effect of H_2SO_4, HNO_3, H_2O_2 oxidation and roasting on sulfide oxidation, carbon oxidation and gold extraction. (Roasting at 750°C; 2 hrs pressure oxidation; conditions similar to those in Figures 10-18)

4.4 PREG-ROBBING ACTIVITY AND LEACHING KINETICS

Figure 20 illustrates the preg-robbing activities of the various residues after pretreatment, as compared to the untreated concentrate. It is observed from this figure that the roasted concentrate shows little or no preg-robbing activity, while the activities for the acid treated residues are similar after two hours, and approach the activity of the untreated sample after six hours. The preg-robbing activity of the peroxide treated residue is significantly less than those of the acid residues throughout the time range investigated.

These results further support the concept of some kind of deactivation of the carbonaceous material by hydrogen peroxide pretreatment. The high preg-robbing activity of the untreated concentrate and those from the acid pretreatment explain the relatively low extraction of gold from these samples during cyanidation. These results also suggest that the preg-robbing activity due to the carbonaceous material is the predominant refractory phenomenon in this double-refractory concentrate.

Figure 21 illustrates the leaching kinetics of untreated concentrate, pressure oxidation residues and roaster discharge. As expected, the leaching rates are fast within the first 2 hours of cyanidation for all the samples. For the untreated concentrate no increase in % extraction was observed after the first 2 hours and only 53% is extracted during the 28 hours of leaching. The acid (H_2SO_4 and HNO_3) pretreated residues have similar leaching kinetics although the H_2SO_4 pretreated sample seem to have faster initial leaching kinetics and gave sightly higher extraction after 28 hours of leaching. The peroxide residue gave higher leaching kinetics and higher gold extraction than the acid treated residues. About 83% of the gold was extracted after 28 hours of leaching. From Figure 21, it is observed that the roasted sample have the fastest leaching kinetics and highest gold extraction for the leaching time investigated.

These results clearly demonstrate that roasting is the best pretreatment method for this double-refractory concentrate, i.e. without considering the environmental implications associated with this pretreatment method. In an attempt to reduce or eliminate the emission

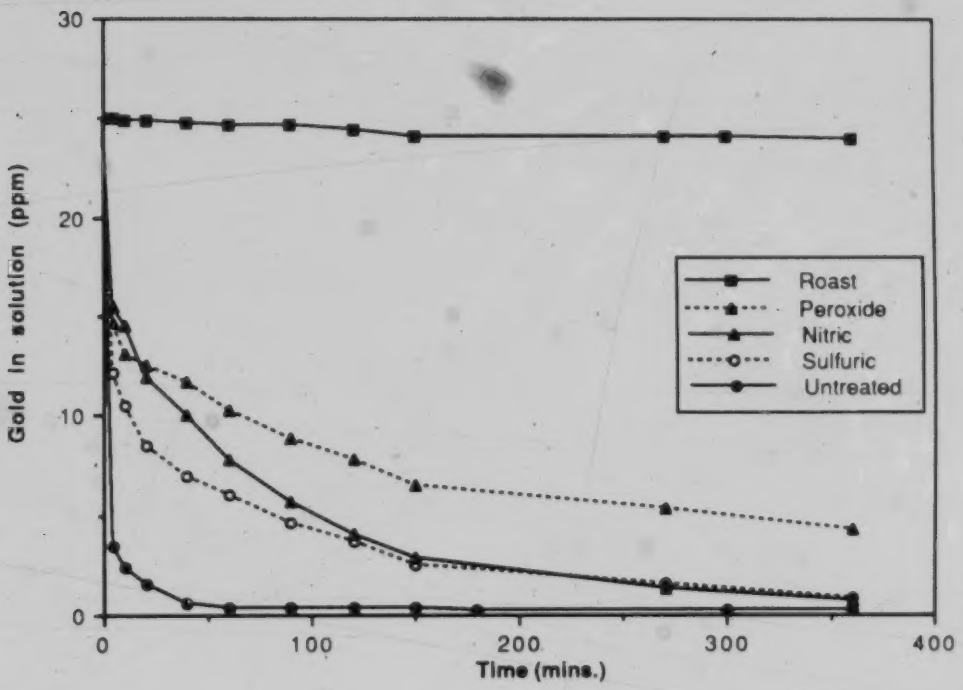

Figure 20. Preg-robbing activities of pressure oxidation residues, untreated concentrate and roaster discharge. (Roasting at 750°C; 2 hrs pressure oxidation; conditions similar to those in Figures 10-18)

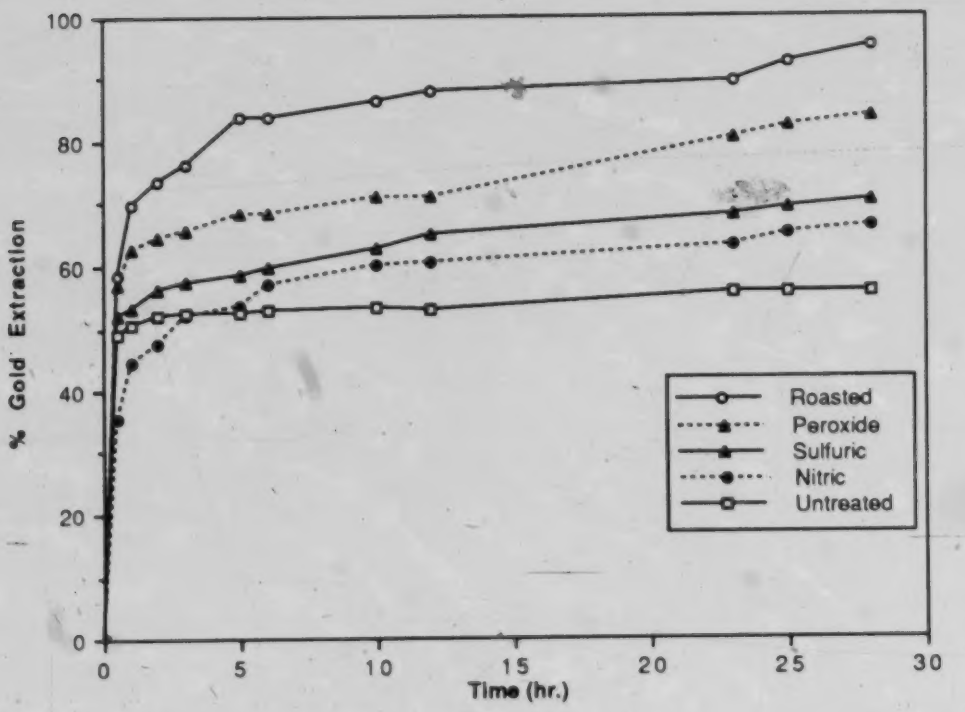

Figure 21. Leaching kinetics of pressure oxidation residues, untreated concentrate and roaster discharge. (Roasting at 750°C; 2 hrs pressure oxidation; conditions similar to those in Figures 10-18)

of the environmentally toxic sulfur dioxide and arsenic trioxide during the roasting of this concentrate, a novel lime agglomeration roast (LAR) pretreatment process was investigated. The result of the LAR pretreatment study are presented in the next Section (Section 4.5).

4.5 LIME AGGLOMERATION ROAST PRETREATMENT

4.5.1 SULFUR DIOXIDE CAPTURE

Dry physical mixing of $Ca(OH)_2$ and the carbonaceous concentrate samples using a wrist shaker produced homogeneous agglomerates suitable for the LAR pretreatment.

To establish the roasting temperature for optimum sulfur dioxide capture, concentrates agglomerated at Ca:S mole ratios between 0.5 to 2.0 were roasted at temperatures between 500°C and 800°C, and the percentage sulfur dioxide capture determined. The results of the effect of temperature at Ca:S mole ratios of 0.5, 1.0, 1.5 and 2.0 are shown in Figures 22 - 25 respectively.

Figure 22 shows that, at a Ca:S mole ratio of 0.5, the sulfur dioxide capture increases from 38% (at 500°C) to 44% (at 700°C) and then decreases slightly to 38% (at 800°C). The temperature effect at a Ca:S mole ratio of 1.0 is shown in Figure 23. The trend of sulfur dioxide capture is observed to be the same as that for Ca:S mole ratio of 0.5 (Figure 22) except the capture at 700°C and 800°C are similar (80%).

Figure 24 (Ca:S mole ratio of 1.5) and Figure 25 (Ca:S mole ratio of 2.0) also show the same trend of the sulfur dioxide capture increasing as the temperature is increased to 700°C and then remains almost constant to 800°C. For Ca:S mole ratios of 1.5 and 2.0 (Figure 24 and 25), the sulfur dioxide capture increased from 87% (at 500°C) to 94% (at 700°C) and from 93% (at 500°C) to 96% (at 700°C) respectively.

From these figures, 700°C seems to be the optimum temperature for sulfur dioxide

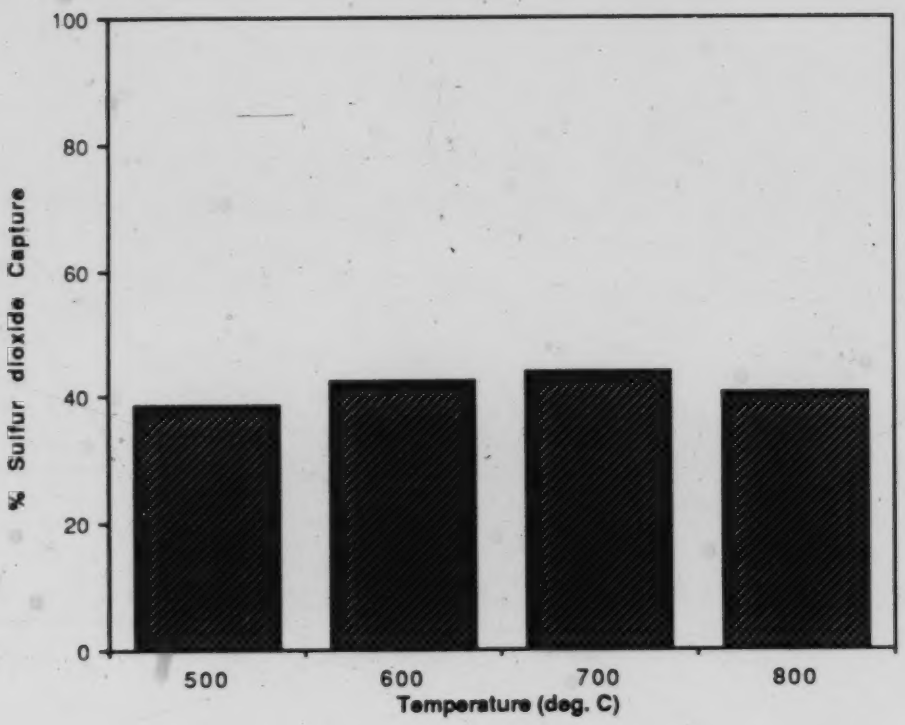

Figure 22. The effect of temperature on sulfur dioxide capture at Ca:S mole ratio of 0.5.

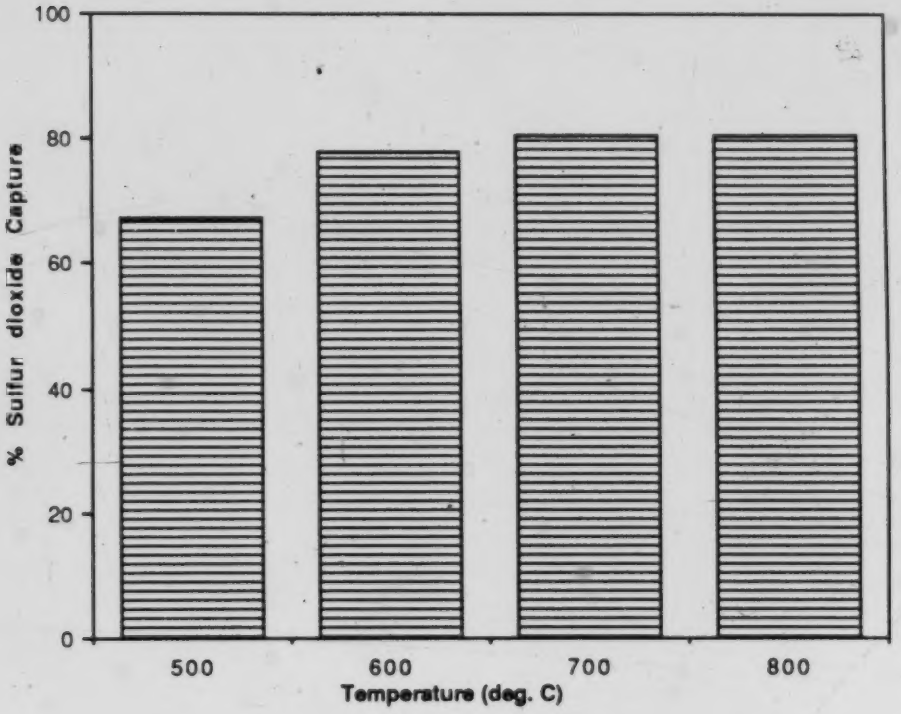

Figure 23. The effect of temperature on sulfur dioxide capture at Ca:S mole ratio of 1.0.

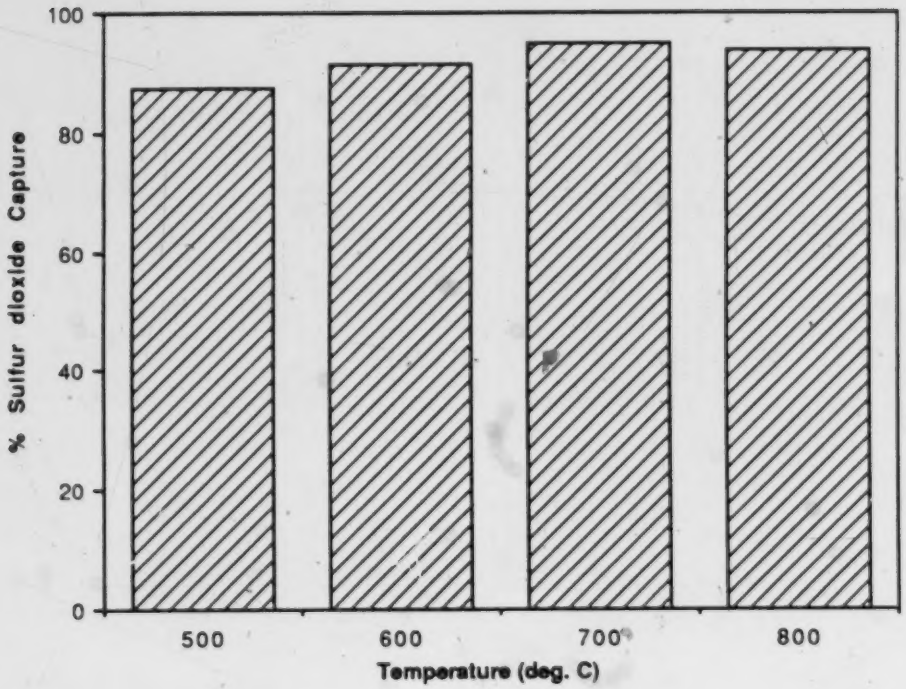

Figure 24. The effect of temperature on sulfur dioxide capture at Ca:S mole ratio of 1.5.

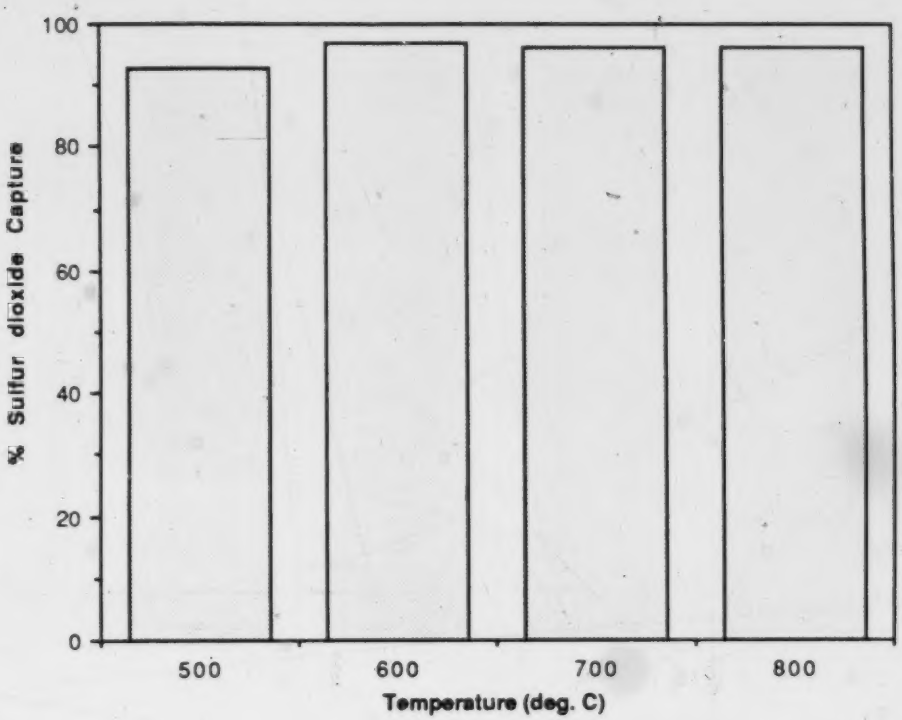

Figure 25. The effect of temperature on sulfur dioxide capture at Ca:S mole ratio of 2.0.

capture since there is not much difference between the capture at 700°C and 800°C for the Ca:S mole ratios investigated.

The effect of Ca:S mole ratio on sulfur dioxide capture at the optimum temperature (700°) is illustrated in Figure 26. As expected, the efficiency of sulfur dioxide capture was observed to increase with increasing Ca:S mole ratio. The sulfur dioxide capture was 43% (at Ca:S mole ratio of 0.5), 80% (at Ca:S mole ratio of 1.0), 95% (at Ca:S mole ratio of 1.5) and 96% (at Ca:S mole ratio of 2.0). Since there is no difference between the capture at Ca:S mole ratios of 1.5 and 2.0, mole ratio of 1.5 is chosen as the optimum Ca:S mole ratio for the concentrate.

The trends are comparable to those obtained by earlier investigators who used lime for the control of sulfur dioxide emission during combustion of Syncrude and Suncor cokes [147]. These results clearly indicate that the LAR pretreatment process can be used to drastically reduce SO_2 emissions, during the roasting of this concentrate, to environmentally acceptable levels.

4.5.2 SULFUR DIOXIDE CAPTURE MECHANISM

During the LAR pretreatment, water rejection from hydrated lime ($Ca(OH)_2$) precedes sulfation. Hence CaO, rather than $Ca(OH)_2$, takes part in the sulfation reaction. The ability of calcium hydroxide to absorb sulfur dioxide is mainly due to the reaction between SO_2, O_2, and CaO to form stable $CaSO_4$ (anhydrite) according to the equations [147]:

$$S_{(g)} + O_{2(g)} \text{ ----> } SO_{2(g)} \qquad (1)$$

$$2CaO_{(s)} + 2SO_{2(g)} + O_{2(g)} \text{ ----> } 2CaSO_{4(s)} \qquad (2)$$

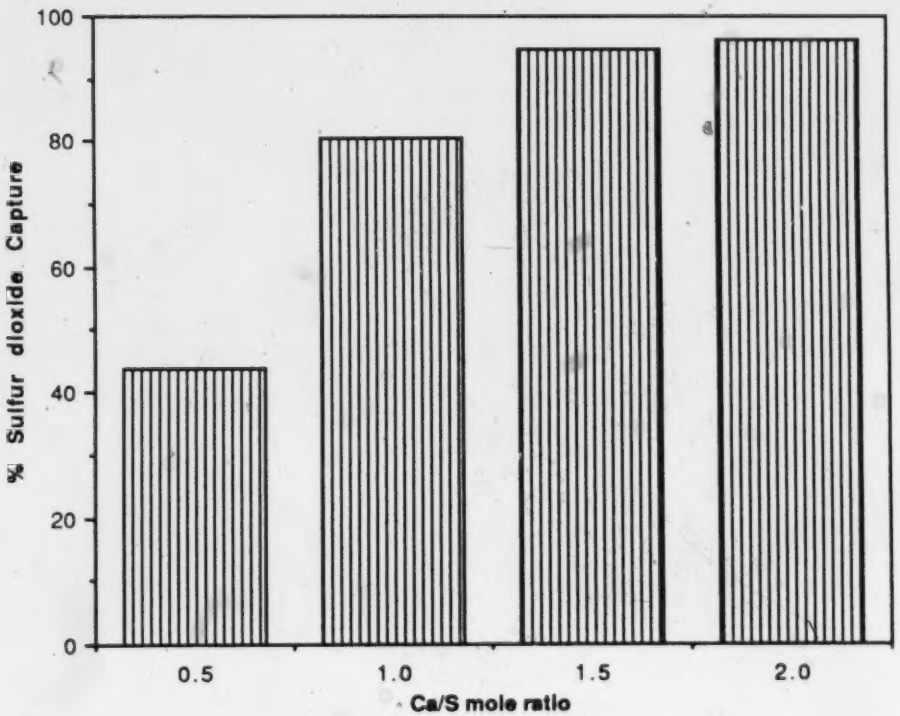

Figure 26. The effect of Ca:S mole ratio on sulfur dioxide capture at optimum temperature (700°C).

Other reactions which occur to a greater or lesser extent during the LAR pretreatment are:

$$CaO_{(s)} + H_2S_{(g)} \text{ ----> } CaS_{(s)} + H_2O_{(g)} \quad (4)$$

$$CaS_{(s)} + 2\,O_{2(g)} \text{ ----> } CaSO_{4(s)} \quad (5)$$

The major product of this sulfur dioxide capture reactions is anhydrite ($CaSO_4$) which is a stable solid residue that can be disposed by conventional methods or used for the production of commercial grade gypsum ($CaSO_4.nH_2O$).

4.5.3 ARSENIC TRIOXIDE CAPTURE

The roasting temperature for optimum arsenic trioxide capture was determined by roasting the agglomerates with Ca:S mole ratios of between 0.5 to 2.0 at temperatures between 500°C and 800°C, and determining the arsenic trioxide capture.

The results of these experiments using Ca:S mole ratios of 0.5, 1.0, 1.5 and 2.0 are illustrated in Figures 27-30 respectively. These Ca:S mole ratios are equivalent to Ca:As mole ratios of 3.2, 6.3, 9.5 and 12.6, respectively. The arsenic trioxide capture follows the same trend for all Ca:S mole ratios investigated. The arsenic trioxide capture increases with increase in temperature from 500°C to 700°C and then decreases from 700°C to 800°C. At Ca:S mole ratio of 0.5 (Figure 27), 28% (at 500°C), 72% (at 600°C), 74% (at 700°C) and 25% (at 800°C) were captured. In Figure 28 (Ca:S mole ratio of 1.0), 51% (at 500°C), 76% (at 600°C), 81% (at 700°C) and 47% (at 800°C) were captured. The arsenic capture for Ca:S mole ratios of 1.5 (Figure 29) and 2.0 (Figure 30) seem to be almost the same for the various temperatures. The captures were 53% (at 500°C), 76% (at 600°C), 84% (at 700°C) and 68% (800°C) for both 1.5 and 2.0 Ca:S mole ratios. From these figures it is observed that 700°C is the optimum temperature for arsenic trioxide capture

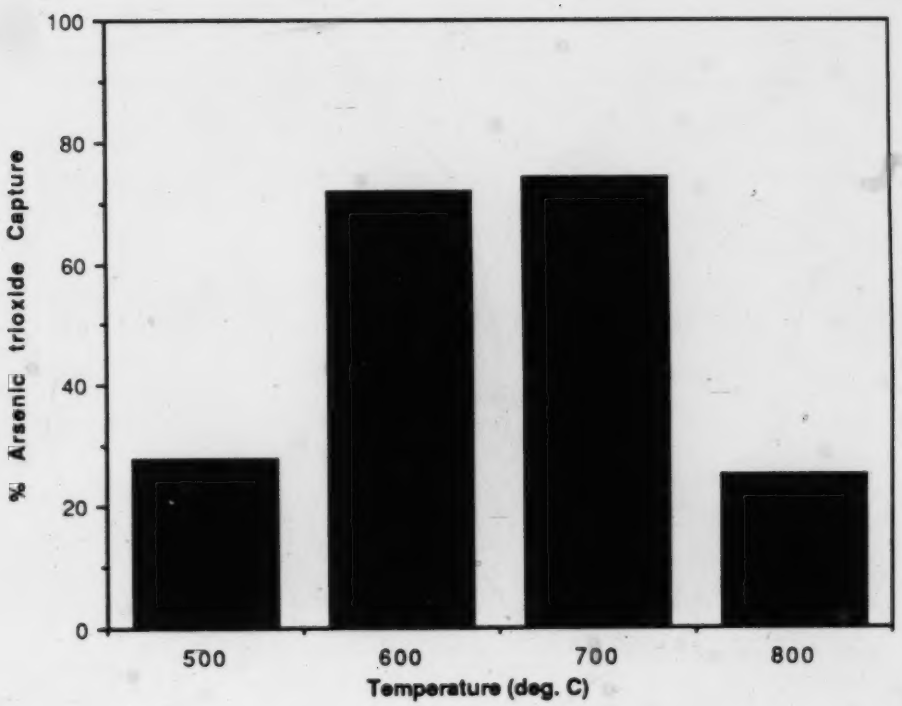

Figure 27. The effect of temperature on arsenic trioxide capture at Ca:S mole ratio of 0.5.

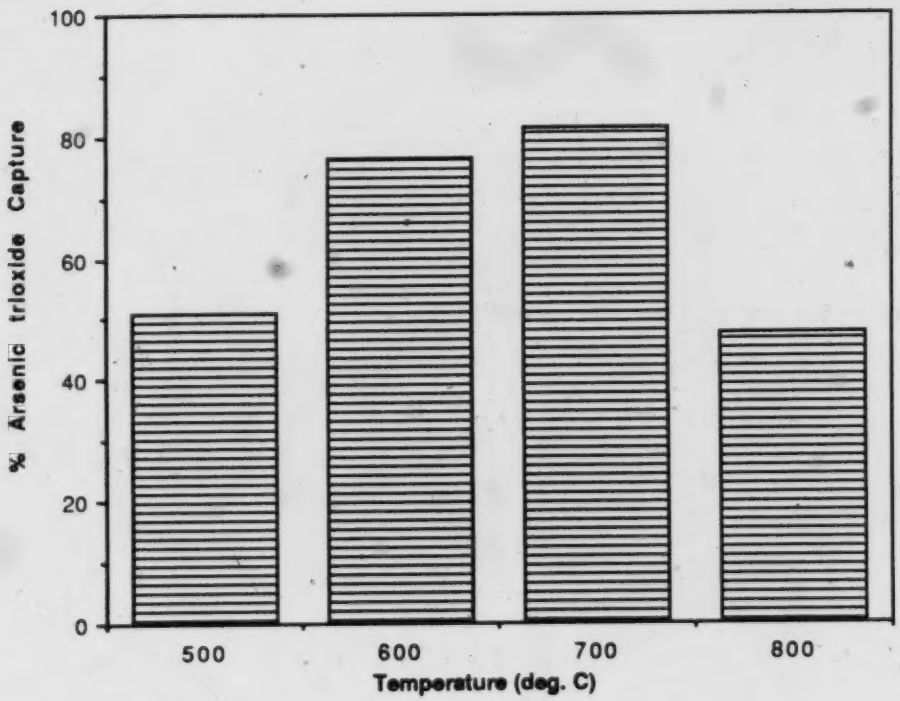

Figure 28. The effect of temperature on arsenic trioxide capture at Ca:S mole ratio of 1.0.

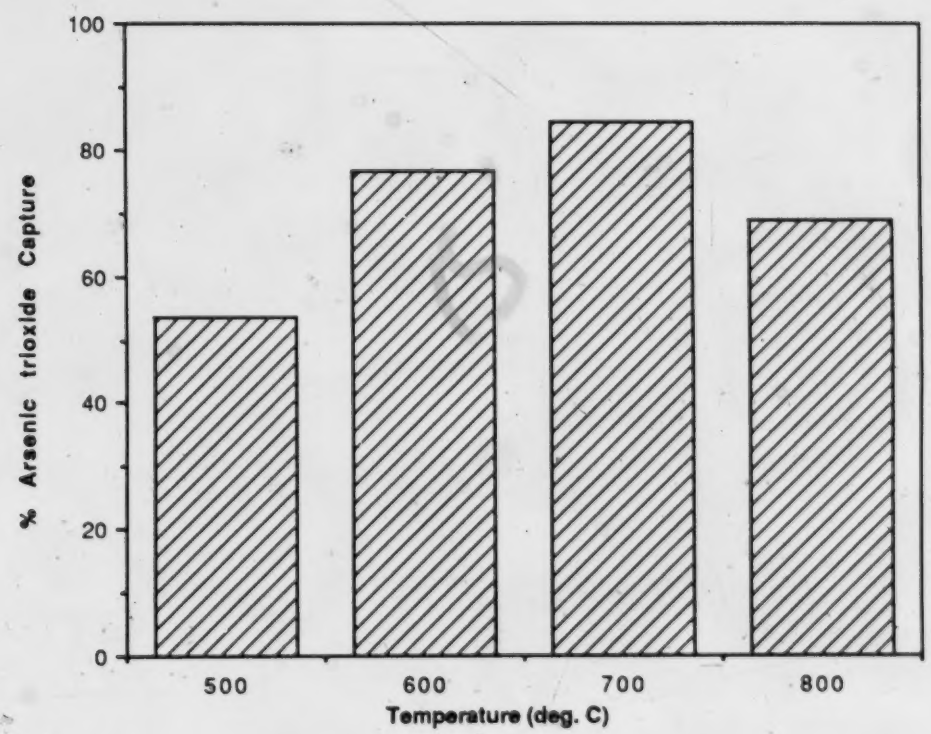

Figure 29. The effect of temperature on arsenic trioxide capture at Ca:S mole ratio of 1.5.

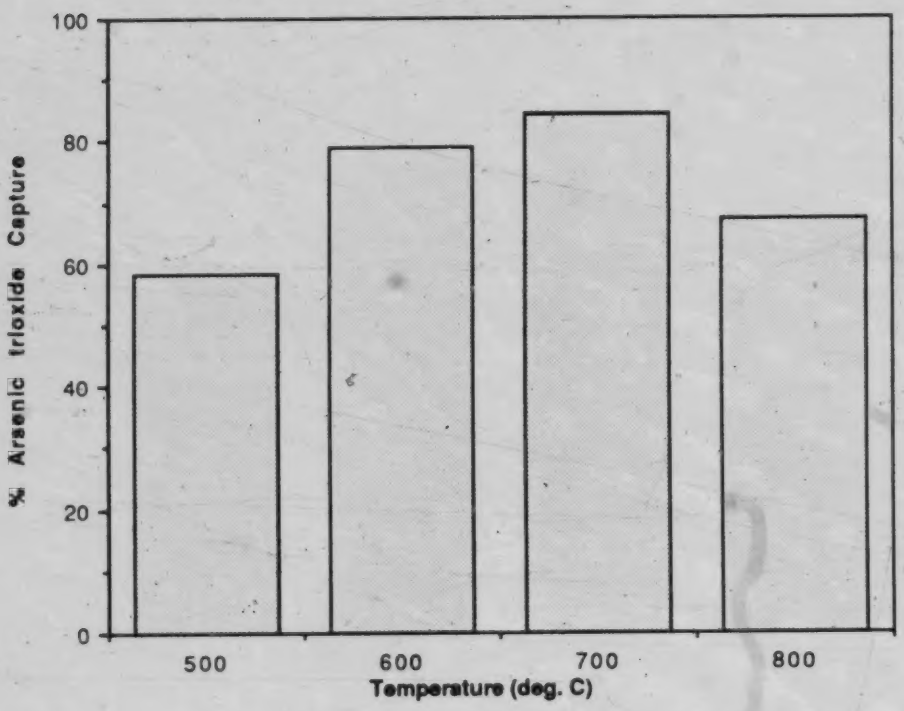

Figure 30. The effect of temperature on arsenic trioxide capture at Ca:S mole ratio of 2.0.

from the concentrate. The possible reasons for the reduction in arsenic trioxide capture are discussed below.

Figure 31 illustrates the effect of Ca:S mole ratio on arsenic trioxide capture at optimum temperature (700°C). The arsenic trioxide capture increases with increase Ca:S mole ratio, but there seems to be not much difference between the capture at mole ratios of 1.5 and 2.0.

The observed increase in percent arsenic trioxide capture with increase in temperature may be due to energy necessary to form calcium arsenate and arsenite which are the main compounds formed during the capture of arsenic. From the trends observed in Figures 27-30, it appears that this compound is stable at temperatures between 650°C and 750°C. The decrease in arsenic trioxide capture at 800°C may be due to partial decomposition of the calcium arsenate and arsenite formed, and the decrease in the amount of active calcium available for surface reaction with arsenic trioxide as a result of sintering at higher temperatures [148]. Furthermore, at higher roasting temperatures, the rate of arsenic trioxide evolution from the concentrate will be much higher. If the rate of arsenic trioxide evolution exceeds the rate of reaction between As_2O_3 and sorbent (i.e., rate of As_2O_3 capture), the activity of the sorbent will show a decrease in As_2O_3 capture. Hence the observed decrease in As_2O_3 capture activities at temperatures higher than 700°C may be attributable to these three phenomena.

4.5.4 ARSENIC TRIOXIDE CAPTURE MECHANISM

The ability of calcium hydroxide to fix arsenic is largely due to the reaction between As_2O_3, O_2, and CaO to form stable calcium arsenate ($Ca_3(AsO_4)_2$) or calcium arsenite $Ca(AsO_2)_2$ according to the equations:

$$4As_{(g)} + 3O_{2(g)} \longrightarrow 2As_2O_{3(g)} \qquad (1)$$

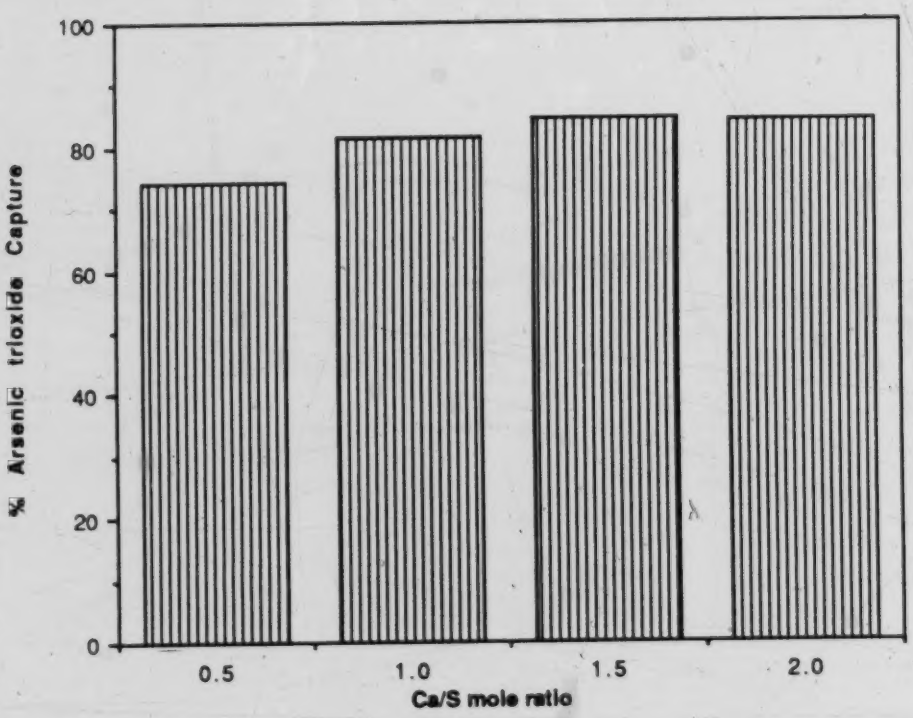

Figure 31. The effect of Ca:S mole ratio on arsenic trioxide capture at optimum temperature (700°C).

$$3CaO_{(s)} + As_2O_{3(g)} + O_{2(g)} \longrightarrow Ca_3(AsO_4)_{2(s)} \quad (2)$$

$$CaO_{(s)} + As_2O_{3(g)} \longrightarrow Ca(AsO_2)_{2(s)} \quad (3)$$

Other reactions which may occur to a greater or lesser extent during the arsenic capture are :

$$As_{2(g)} + O_{2(g)} \longrightarrow 2AsO_{(g)} \quad (4)$$

$$3CaO_{(s)} + 2AsO_{(g)} + 3/2\ O_{2(g)} \longrightarrow 3CaO.As_2O_{5(s)} \quad (5)$$

$$4AsO_{(g)} + O_{2(g)} \longrightarrow As_4O_6 \quad (6)$$

$$2CaO_{(s)} + 1/2\ As_4O_{6(g)} + O_2 \longrightarrow 2CaO.As_2O_{5(s)} \quad (7)$$

4.5.5 OPTIMUM EMISSION CONTROL PARAMETERS

The results of the temperature and Ca:S mole ratio effects on SO_2 and As_2O_3 capture efficiency of the agglomerates suggest that roasting of refractory gold concentrates agglomerated with $Ca(OH)_2$ may be done without causing serious environmental damage (i.e. SO_2 and As_2O_3 emissions). For the double-refractory concentrate being used, agglomerating with $Ca(OH)_2$ to Ca:S mole ratio of 1.5, and roasting at 700°C gives optimum capture results with respect to SO_2 and As_2O_3 emission control.

4.5.6 CYANIDATION OF LAR RESIDES

Since the optimum goal of roasting the concentrate is to extract as much gold as possible and not only to control emissions, the residues from the LAR pretreatment were leached with alkaline cyanide to investigate the effect of the agglomeration on the extraction

of gold. The residues were also analyzed for carbon since preliminary roasting at 750°C (so as to compare gold extractions from pressure oxidation residues) had shown that complete oxidation of the carbon was necessary to achieve good gold extraction.

Figure 32 illustrates the effect of roasting temperature on % carbon oxidation. As expected, the carbon oxidation increases with temperature. At a temperature of 700°C, almost complete oxidation (97%) of the carbon is achieved. The effect of the roasting temperature on the % gold extraction from the residues (without $Ca(OH)_2$ agglomeration) is also shown in Figure 33. The gold extraction increases with roasting temperature, from 75% (at 500°C) to 95% (at 700°C), and then decreases to 86% as the temperature is increased to 800°C. This observation is in general agreement with the literature on the roasting behavior of refractory concentrates. The trend is attributed to the incomplete oxidation of the sulfides and carbonaceous materials at low temperatures (below 600°C), and the formation of less porous (dense) residues at temperatures above 700°C [149].

The effect of Ca:S mole ratio on the gold extraction from the LAR residues pretreated at temperatures of 500°C, 600°C, 700°C and 800°C are shown in Figures 34-37, respectively. For roasting at 500°C (Figure 34), and 600°C (Figure 35), the % gold extraction decreased with increase in Ca:S mole ratio. For roasting at 700°C (Figure 36), the gold extraction did not vary much with increase in Ca:S mole ratio as compared to the other temperatures. However, an insignificant decrease in % gold extraction is observed between Ca:S mole ratios of 1.0 and 1.5. The generally low levels of gold extractions at temperatures below 700°C (i.e. 500°C and 600°C) at all Ca:S mole ratios may be attributable to the preg-robbing activities of the residual carbonaceous materials (Figure 32). The reasons for the substantial decrease in gold extraction with increasing Ca:S mole ratios for the samples roasted at 500°C and 600°C is not clear at this time. Gold extractions at all Ca:S mole ratios for the concentrate roasted at 700°C were well above 90% (Figure 36) and are quite comparable to the level of gold extraction obtained for the concentrate roasted at 700°C in the absence of lime.

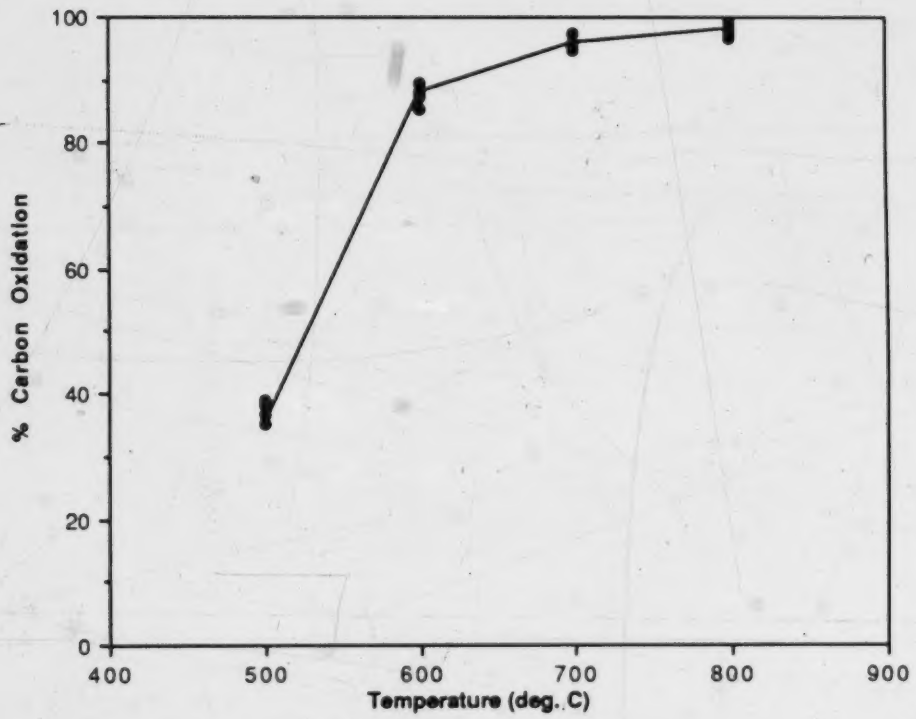

Figure 32. The effect of roasting temperature on oxidation of carbonaceous materials in refractory gold concentrate.

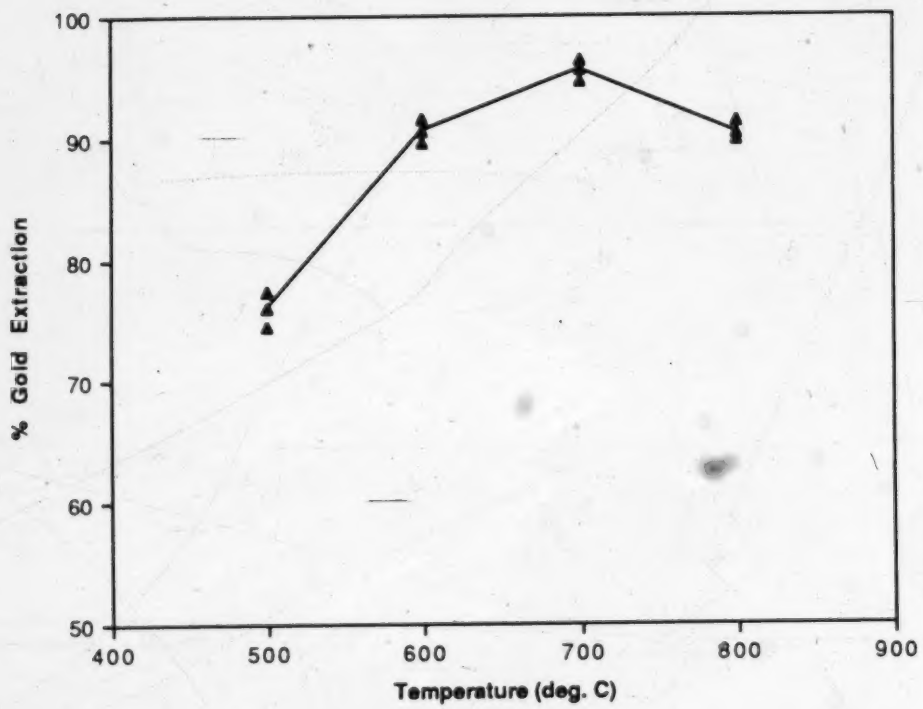

Figure 33. The effect of roasting temperature on % gold extraction (no lime agglomeration prior to roasting).

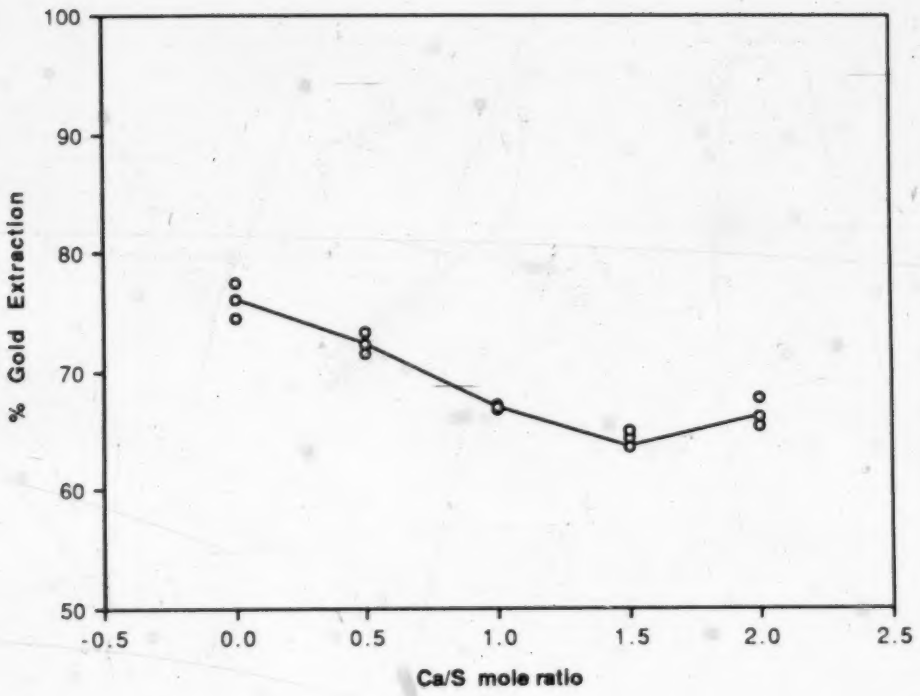

Figure 34. The effect of calcium hydroxide addition on % gold extraction (roasting temperature of 500°C).

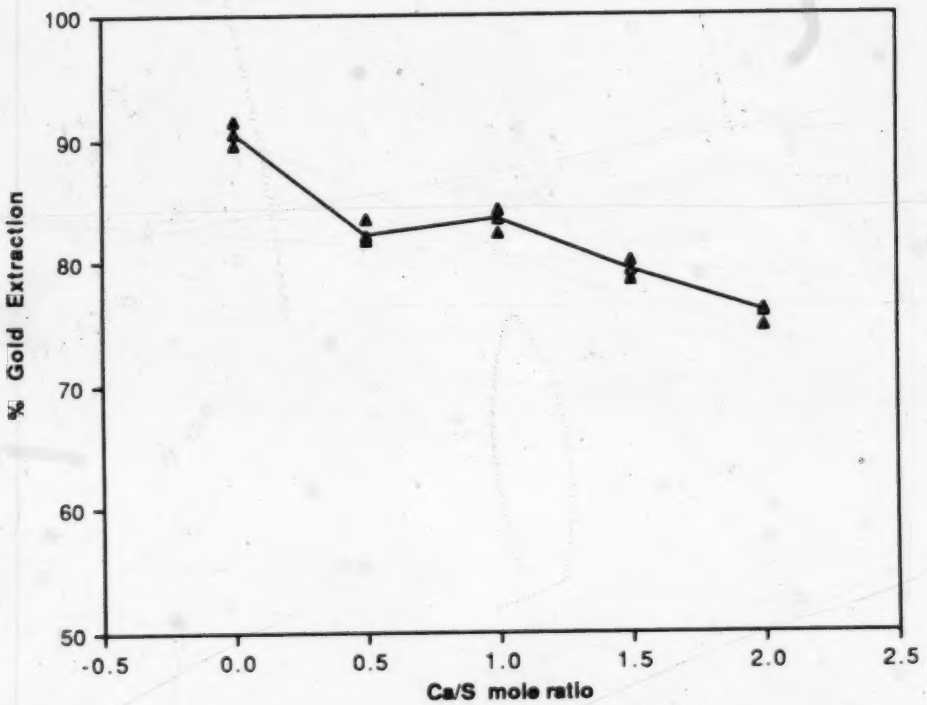

Figure 35. The effect of calcium hydroxide addition on % gold extraction (roasting temperature of 600°C).

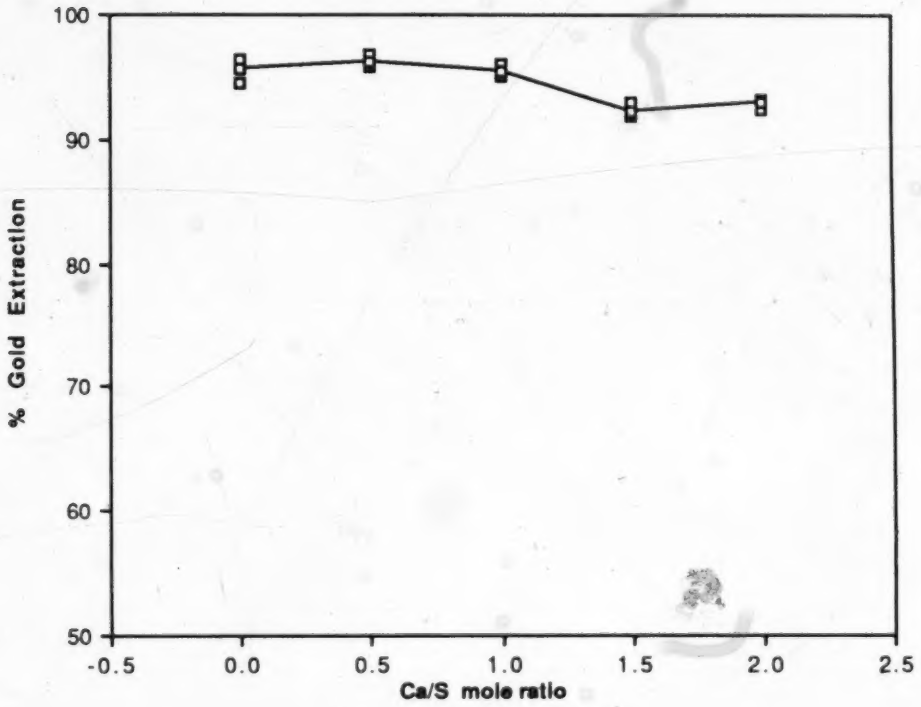

Figure 36. The effect of calcium hydroxide addition on % gold extraction (roasting temperature of 700°C).

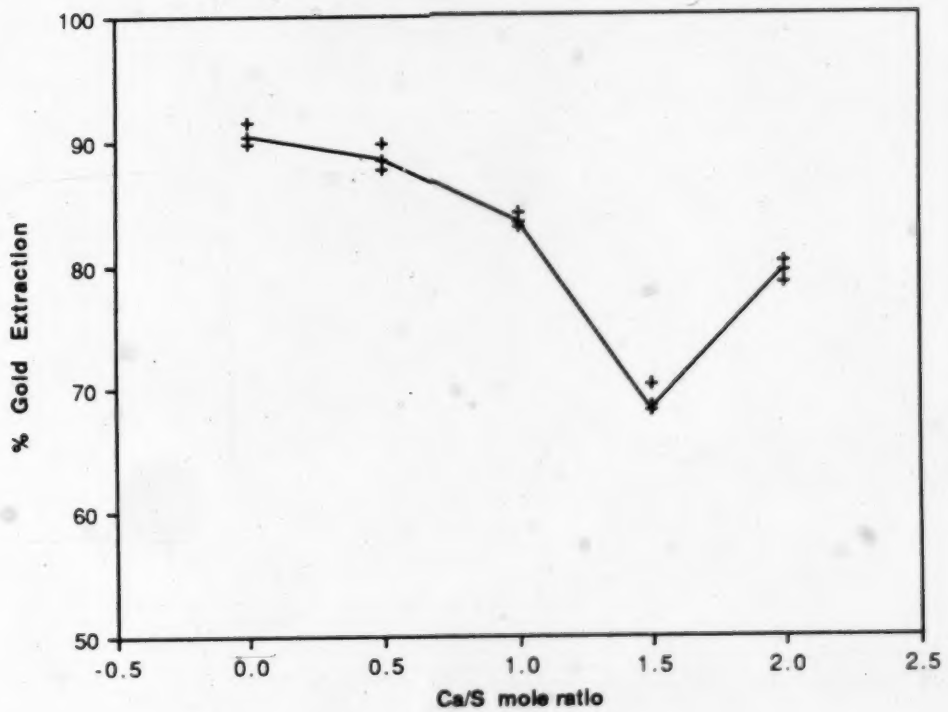

Figure 37. The effect of calcium hydroxide addition on % gold extraction (roasting temperature of 800°C).

These results show that at the optimum LAR conditions of 700°C and Ca:S mole ratio of 1.5, no deleterious effects regarding % gold extraction were observed. The LAR pretreatment show major environmental advantages in terms of reduction in SO_2 and arsenic trioxide emission.

The greatest variation in gold extraction with increasing Ca:S mole ratio was observed at 800°C (Figure 37). At this temperature anomalies were observed as the gold extraction decreased from 90% (no $Ca(OH)_2$ addition) to 70% (at Ca:S mole ratio of 1.5) and increased to 80% (at Ca:S mole ratio of 2.0). The reason for these anomalies is not known. The general decrease in gold extractions with increasing Ca:S mole ratios for samples roasted at 800°C is attributable to the formation of less porous and sintered residues at temperatures above 700°C [149]. These dense residues can occlude the fine gold particles and reduce the access of the cyanide lixiviant.

It was observed that during cyanidation of LAR residues with Ca:S mole ratio above 1.0, lime was not needed for neutralization before cyanidation since pHs of the 10% slurries prepared were above 10.5. This means the lime used for agglomeration had served a dual purpose of fixing sulfur and arsenic, and also neutralization of the slurry.

4.5.7 ARSENIC IN FINAL LEACH SOLUTION

Since the LAR pretreatment fixes arsenic in the roaster discharge, the final cyanide leach solutions of the residues were analyzed for arsenic to determine if the arsenic is leached into solution, which would make it necessary to treat the solution after gold recovery.

Figures 38-41 show the effect of Ca:S mole ratio on the % arsenic content of the final leach solution for roasting temperatures of 500°C, 600°C, 700°C and 800°C respectively. The % arsenic was calculated based on arsenic content of roaster discharges and the cyanidation residues. Because of the fluctuations in the arsenic values, best fit lines were drawn to show trends.

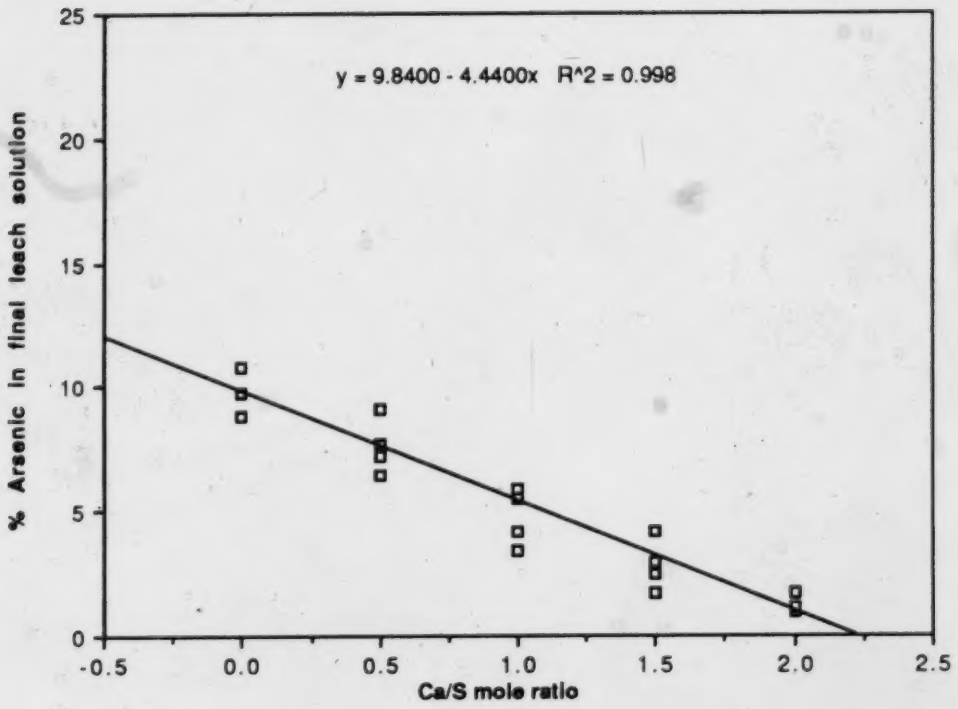

Figure 38. The effect of calcium hydroxide addition on % arsenic content of the final leach solution (roasting temperature of 500°C).

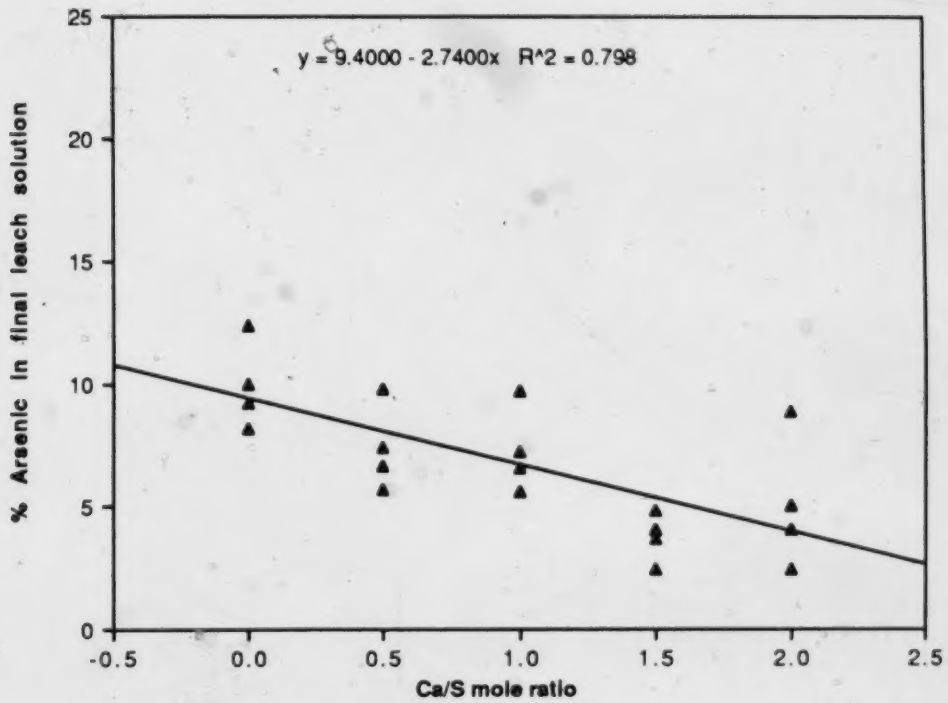

Figure 39. The effect of calcium hydroxide addition on % arsenic content of the final leach solution (roasting temperature of 600°C).

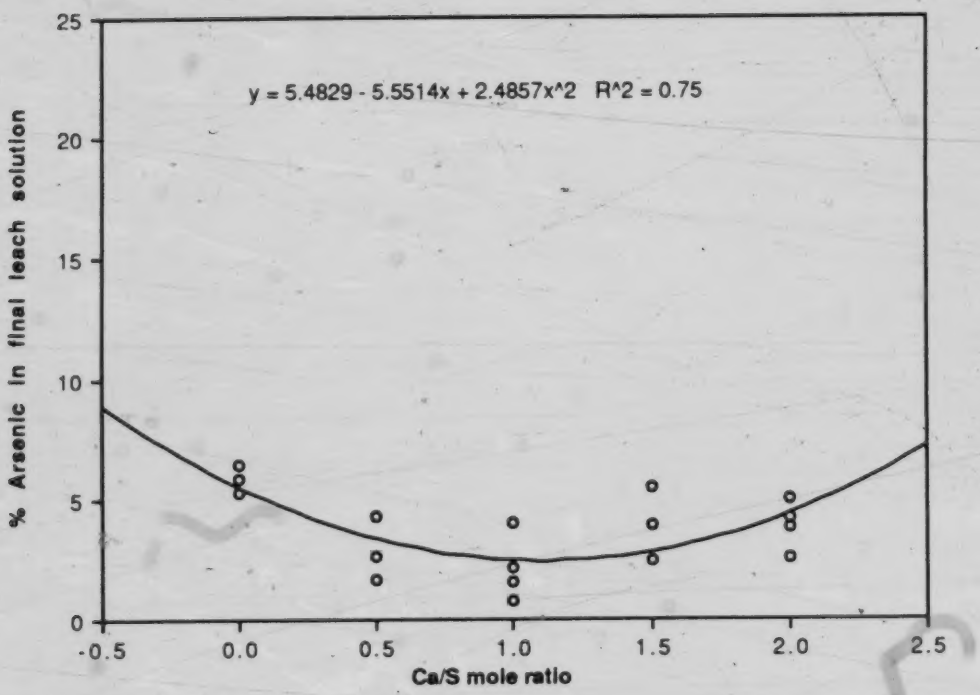

Figure 40. The effect of calcium hydroxide addition on % arsenic content of the final leach solution (roasting temperature of 700°C).

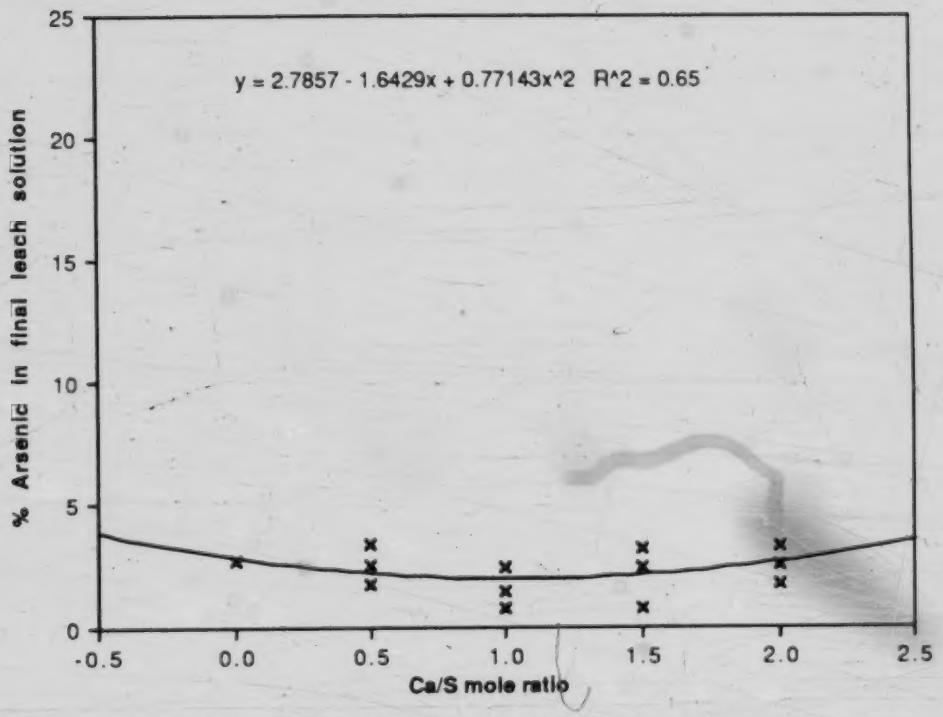

Figure 41. The effect of calcium hydroxide addition on % arsenic content of the final leach solution (roasting temperature of 800°C).

For all the temperatures and Ca:S mole ratios experimented, it was observed that less than 15% of the initial arsenic was leached into solution. The Ca:S mole ratio of 0.0 represents concentrates without agglomeration; most of the arsenic in this concentrate was actually driven off during the roasting.

At 500°C (Figure 38), the % arsenic leached into solution decreased as the Ca:S mole ratio was increased. At this temperature, with Ca:S mole ratios above 1.0, less than 5% of the initial arsenic was leached into solution. For 600°C (Figure 39), the same trend was observed although slightly higher % arsenic was leached into solution. For roasting temperatures above 500°C, the % arsenic leached into solution do not seem to vary much as the Ca:S mole ratios are increased from 0.5 to 2.0, though less than 10% is leached. At 700°C (Figure 40), the % arsenic leached into solution seemed to decrease as the Ca:S mole ratio was increased from 0.0 to 1.0, and increased slightly with increase in Ca:S mole ratio from 1.0 to 2.0. The % arsenic leached into solution at this temperature was still below 5% for all mole ratios investigated. At 800°C (Figure 41) the % arsenic leached into solution does not seem to change with Ca:S mole ratio. Less than 4% arsenic was leached into solution.

Stefanakis and Kontopoulos [150] who studied the effect of Ca:As mole ratio and calcination temperature on calcium arsenite and arsenate also observed that the arsenic solubility in a solution of pH 11.5 decreased with increasing Ca:As mole ratio. The arsenic solubility was also observed to decrease with increase in calcination temperature.

It is inferred from the above figures that, the arsenic fixed during the LAR pretreatment is not leached into solution during cyanidation. This means that there will be no need to treat barren solution for arsenic removal after gold precipitation.

4.5.8 DISPOSAL OF LAR CYANIDATION RESIDUE

There has been disagreements in the literature regarding whether or not both calcium arsenites and arsenates are appropriate forms of compounds for arsenic

stabilization [137, 139]. There is also controversy over arsenic stabilization as scorodite during pressure oxidation [140, 141]. However, it has been reported by Nishimura et. al. [151] and Stefanakis [150] that under certain conditions, with respect to Ca:As ratios and calcination temperature, both calcium arsenites and arsenate become very insoluble and therefore constitute effective arsenic stabilization compounds.

Since the anhydrite ($CaSO_4$) formed is also very stable [152], and the calcium arsenite and arsenate formed become very stable after calcination at the temperatures used during roasting, the LAR cyanidation residue could be disposed of in an environmentally acceptable manner without further treatment. The barren solution after the precipitation of gold does not need to be treated for arsenic removal since most of the arsenic remains in the residue. A general flowsheet for treating refractory gold ores and concentrate which incorporates the LAR pretreatment process is presented in Figure 42.

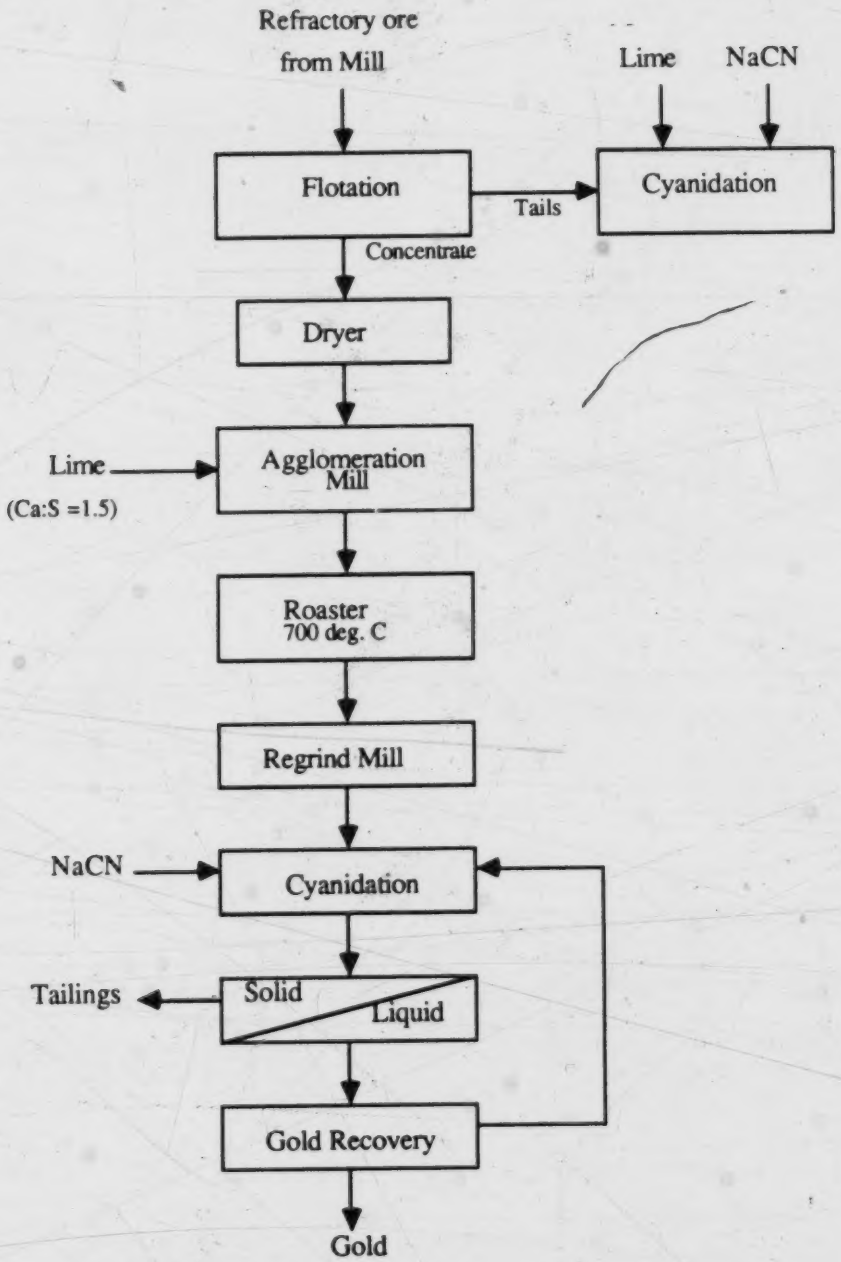

Figure 42. LAR pretreatment and cyanidation flowsheet for treating refractory gold ores and concentrates.

5. CONCLUSIONS

The extraction of gold from a double-refractory concentrate was studied using Carbon-in-leach, Resin-in-leach, Pressure oxidation, Roasting and Lime Agglomeration Roast pretreatment processes.

The results of the study have shown that the concentrate contains hydrocarbon and graphitic materials capable of adsorbing gold cyanide complex from solution. Particle size and SEM analysis have shown that gold, sulfides and carbonaceous materials are very fine and intimately associated, and therefore cannot be separated into different fractions.

Fire assay and chemical analysis have shown that the concentrate contained significant content of gold, carbon, sulfur and arsenic. The high sulfur and arsenic suggest that direct roasting of the concentrate as a pretreatment step will be undesirable due to the serious environmental problems.

Carbon-in-leach and Resin-in-leach cyanidation did not result in any significant improvement of gold extraction, because not only does the concentrate exhibit preg-robbing activity but the fine gold particles are also occluded by sulfide and carbon materials, and is not accessible by the cyanide solution. The high aluminium content also showed that the concentrate contained high clay contents capable of deactivating adsorbents added during the in-pulp and in-leach processes. These properties are evidence of the double-refractory nature of the concentrate.

The results of this study have also shown that sulfuric and nitric acid pressure oxidation pretreatments do not oxidize the carbonaceous materials in refractory gold ores or concentrates as efficiently as the sulfide content. The oxidation of the sulfur content of the double-refractory concentrate studied here, results in an improvement in gold extraction during subsequent cyanidation, but some deactivation or complete removal of the carbon content is required before gold extractions above 80% can be achieved.

The residues obtained from acid pressure oxidation show preg-robbing activities which are similar to those of the untreated concentrate. Only residues from the roasting pretreatment did not show any preg-robbing activity. While the use of hydrogen peroxide results in low sulfur and carbon oxidation, it reduces the preg-robbing activity of the carbon, leading to significantly higher gold extraction during cyanidation.

It can be concluded from these results that the preg-robbing activity, due to the carbon content of this concentrate, is the predominant phenomenon relative to sulfide mineral occlusion of gold particles. The results also show that only roasting pretreatment is capable of oxidizing completely the carbonaceous materials in the concentrate, resulting in high gold extraction during subsequent cyanidation. However, due to sulfur dioxide and arsenic emission, a direct roasting pretreatment process will not be environmentally acceptable.

The results of the novel Lime Agglomeration Roast (LAR) pretreatment study have shown that the sulfide and carbonaceous materials in the concentrate are oxidized completely. The residues from the LAR pretreatment resulted in very high gold extraction since the residues do not contain residual carbonaceous materials and therefore do not exhibit preg-robbing activities. At the optimum LAR conditions of 700°C and Ca:S mole ratio of 1.5, above 90% gold extraction is obtained from this double-refractory concentrate which could not be pretreated with hydrometallugical methods (i.e. Acid Pressure Oxidation).

The lime added during the LAR pretreatment served a dual purpose of fixing sulfur dioxide and arsenic in the roaster discharge, and the neutralization of the slurry during cyanidation. In effect, lime which is usually added to the concentrate after oxidation pretreatment processes (H_2SO_4, HNO_3 Pressure Oxidation, or Roasting) for neutralization of the cyanidation pulp can be added to the concentrate before LAR pretreatment to control sulfur dioxide and arsenic emission problems. This makes the process very cost effective.

Since the sulfur dioxide and arsenic are fixed in the solid as anhydrite ($CaSO_4$), and calcium arsenite and arsenate respectively, and these compounds are not soluble in alkaline cyanide solutions, there will be no need for the treatment of barren solutions for sulfur and arsenic removal after gold precipitation.

Finally, it can be concluded from these results that the LAR pretreatment is an effective process for oxidizing refractory materials in ores and concentrates prior to extraction of the metal values. The technique could be applied to both precious and base metal sulfide and carbonaceous ores and concentrates with major environmental advantages in terms of reduction in sulfur and arsenic emission, and disposal of the leached residues and barren solutions.

6. REFERENCES

1. WEIR, D.R., and BEREZOWSKY, R.M.G.S., Gold extraction from refractory concentrates; Presented at the 14th Annual Hydrometallurgical meeting of CIM, Timmins, Ontario, October 1984.

2. DEMOPOULOS, G.P., and PAPANGELAKIS, V.G., Acid pressure oxidation of refractory gold mineral carriers; Proceedings of the International Symposium on Gold Metallurgy, Winnipeg, Canada, Pergamon Press, Oxford, pp. 341-357, 1987.

3. ZAITSEVA, M.L., IVANOVSKII, M.D., and LARINA, N.K., An examination of the sorption properties of carbonaceous substances during the cyanidation of gold ores; Soviet Journal of Non-ferrous Metals, Vol. 14, No.1, pp. 78-80, 1973.

4. NICE, R.W., Recovery of gold from active carbonaceous ores at McIntyre; Canadian Mining Journal, Vol. 92, No. 6, pp. 41-49, 1971.

5. SCHEINER, B.J., LINDSTROM, R.E., and HENRIE, T.A., Processing refractory carbonaceous ores for gold recovery; Journal of Metals, Vol. 23, No. 3, pp. 37-40, 1971.

6. EISELE, J.A., COLOMBO, A.F., and McCLELLAND, G.E., Recovery of gold and silver from ores by hydrometallurgical processing; Separation Science and Technology, Vol. 18, pp. 1081-1094, 1983.

7. WELLS, J.D., and MULLENS, T.E., Gold-bearing arsenian pyrite determined by microprobe analysis, Cortez and Carlin Gold Mines, Nevada; Economic Geology, Vol. 68, pp. 187-201, 1973.

8. GASPARRINI, C., The mineralogy of gold and its significance in metal extraction; CIM Bulletin, Vol. 76, No. 851, pp. 144-153, 1983.

9. CHEN, B., and REDDY, R.G., Roasting characteristic of refractory gold ores; Advances in Gold and Silver Processing, Proceedings of the Symposium at GoldTech 4, Reno, Nevada, pp. 201-214, 1990.

10. SCHWARTZ, G.M., The host minerals of native gold; Economic Geology, Vol. 39, No. 6, pp. 371-405, 1944.

11. WEIR, D.R., KING, J.A., and ROBINSON, P.C., Preconcentration and pressure oxidation of Porgera refractory gold ore; Minerals and Metallurgical Processing, Vol. 3, No. 4, pp. 201-208, 1986.

12. PAPANGELAKIS, V.G., and DEMOPOULOS, G.P., Acid pressure oxidation of arsenopyrite Part I, Reaction Chemistry; Canadian Metallurgical Quarterly, Vol. 29, No. 1, pp. 1-12, 1990.

13. MICHAELIS, H.V., Innovative refractory ore treatment processes; Proceedings, Randol Gold Conference, Sacramento, California, pp. 95-102, 1989.

14. SCHWEIGART, H., Solid solution of gold in sulfides; Economic Geology, Vol. 60, pp. 1540-1542, 1965.

15. HAN, K.N., and CHEN, Y., Separation of carbonaceous material from Carlin ore by flotation; Advances in Gold and Silver Processing, Proceedings of the Symposium at GoldTech 4, Reno, Nevada, pp. 121-130, 1990.

16. KUIPERS, J., Novel aspects of gold recovery using column flotation at Austin Gold Venture; Proceedings, Randol Gold Conference, Sacramento, California, pp. 55-57, 1989.

17. SIMMONS, G., Novel selective flotation approach to refractory carbonaceous ore treatment at Royal Mountain King Mine; Randol Gold Conference, Sacramento, California, pp. 59-70, 1989.

18. HAYDED, A. S., MASON, P. G., and YEN, W. T., Refractory gold ore oxidation-Simulation of continuous flow; Proceedings of the International Symposium on Gold Metallurgy, edited by R. S. Salter, D. M. Wyslouzil and G. W. McDonald, pp. 249-258, 1987.

19. BRUNK, K. A., and ATWOOD, R. L., Practical aspects of chlorination of carbonaceous ores; Process Mineralogy VII, Application to Mineral Beneficiation Technology and Mineral Exploration, with Special Emphasis on Disseminated Carbonaceous Gold Ores, pp. 15-27, 1987.

20. SCHEINER, B.J., LINDSTROM, R.E., and HENRIE, T.A., Oxidation process for improving gold recovery from Carbon-bearing gold ores, Report of Investigation, No. 7573, U. S. Bureau of Mines, 1971.

21. GUAY, W.J., The treatment of refractory gold ores containing carbonaceous materials and sulfides; Gold and Silver Leaching, Recovery and Economic, SME-AIME, New York, pp. 17-22, 1981.

22. McQUISTON, F.W. Jr., and SHOEMAKER, R.S., Gold and Silver Cyanidation Plant Practice Monograph, SME-AIME, New York, pp. 11-22, 1975.

23. HISKEY, J.B., and ATLURI, V.P., Resin-in-leach cyanidation of a carbonaceous gold ore; Minerals and Metallurgical Processing, Vol. 6, No. 3, pp. 113-116, 1989.

24. JACKSON, D., Jerritt Canyon project; Engineering and Mining Journal, Vol. 183, No. 7, pp. 54-58, 1982.

25. FRIDMAN, I.D., and SAVARI, E.E., Treating carbon containing Ag-Au-As concentrates; World Mining, Vol. 36, No. 7, pp. 45-47, 1983.

26. BICKER, E., WALL, N.C., and CROWE, M., The introduction of novel Davy CIP technology for the recovery of gold at Ashanti Goldfields, Ghana; Proceedings, Randol Gold Conference, Sacramento, California, pp. 363-369, 1989.

27. GUINIVEREM, R., McLauglin project: Process, Project and Construction Development; Proceedings of the First International Symposium on Precious Metals Recovery, Reno, Nevada, paper no. 14, 1984.

28. WEIR, D.R., and BEREZOWSKY, R.M., Aqueous pressure oxidation of refractory feed stocks; Proceeding of the International Symposium on Gold Metallurgy, Winnipeg, Canada, Pergamon Press, Oxford, pp. 247, 1987.

29. RAUDSEPP, R., PETERS, E., and BEATTIE, M.J.V., Process for recovering gold and silver from refractory ores; U. S. Patent No. 4,647,307, 1987.

30. BEATTIE, M.J.V., RAUDSEPP, R., The Arseno process - An update; Projects '88, Proceedings, 18th Hydrometallurgical meeting, Edmonton, Alberta, Canada, paper no. 3, 1988.

31. HACKL, R. P., Operation of a commercial scale bioleach reactor at the congress gold property; Advance in Gold and Silver Processing Proceedings of the Symposium at GoldTech 4, Reno, Nevada, pp. 131-141, 1990.

32. BRUYNESTEYN, A. and DUNCAN, D. W., Microbiological leaching of sulfide concentrate; Canadian Metallurgical Quarterly, vol. 10, no. 1, pp. 57-63, 1971.

33. MARCHANT, P. B., Commercial piloting and the economic feasibility of plant scale continuous biological tank leaching at Equity Silver Mines Limited; R.W. Lawrence, R. M. R. Branion, and H. E. Ebner (eds.), Fundamental and Applied Biohydrometallurgy, Elsevier, New York, pp. 53-76, 1986.

34. VAN ASWEGEN, P. C., and HAINES, A. K., Bacteria enhance gold recovery; Intern, Min. pp. 19-23, May, 1988.

35. LAWRENCE, R. W., and MARCHANT, P. B., Biochemical pretreatment in arsenical gold ore processing, R. G. Reddy, J. L. Hendrix, and P. B. Queneau (eds.), Arsenic Metallurgy Fundamentals and Applications, Met. Soc., AIME, Warrendale, PA, pp. 199-211, 1988.

36. TSAI, S.C., Fundamentals of coal benefication and utilization, Coal Science Technology Vol. 2, Elsevier, pp. 65-74, 1982.

37. SCHEINER, B. J., Relation of Mineralogy to Treatment Methods for Carbonaceous Gold Ores; Process Mineralogy VII: Applications to Mineral Beneficiation Technology and Mineral Exploration, with Special Emphasis on Disseminated Carbonaceous Gold Ores, pp. 3-12, 1987.

38. JHA, M. C., Refractoriness of certain gold ores to cyanidation: Probable causes and possible solutions; Mineral Processing and Extractive Metallurgy Review, vol. 2, pp. 331-352, 1987.

39. JHA, M. C., and KRAMER, M. J., Recovery of gold from arsenical ores; Precious Metals: Mining, Extraction, and Processing, V. Kudryk, D. A. Corrigan and W. W. Liang (eds.) pp. 337-365, 1984.

40. ROBIE, E. H., Producing Gold and Arsenic at Jardine, Montana; Engineering and Mining Journal Press, pp. 765-772, Nov. 14, 1925.

41. HABER, W. G., and MARTIN, F. J., Ore treatment at Beattie Gold Mines Limited; AIME Transactions, vol. 112, pp. 690-703, 1934.

42. MATTEWS, O., Cochenour Williams Mill; Engineering and Mining Journal, pp. 45-47, March 1942.

43. BARR, D. S., BIRAK, D. J., McCORD, T. H., and O'NEIL, G. R., The various forms of refractoriness in Nevada gold ores; Process Mineralogy VII: Applications to Mineral Beneficiation Technology and Mineral Exploration, with Special Emphasis on Disseminated Carbonaceous Gold Ores, pp. 81-97, 1987.

44. YANNOPOULOS, J. C., The Extractive Metallurgy of Gold; Van Nostrand Reinhold, New York, 1991.

45. BOYLE, R. W., The Geochemistry of Gold and its Deposits; Geological Survey of Canada Bulletin, No. 280, 1979.

46. JORALEMON, P., The occurrence of gold at the Getchell Mine Nevada; Economic Geology, vol. 46, no. 3, pp. 267-309, 1951.

47. HAYCOCK, M. H., The role of the microscope in the study of gold ores; Canad. Inst. Min. Met., vol. 40, pp. 405-414, 1937.

48. STILLWILL, F. L., and EDWARDS, A. B., An occurrence of submicroscopic gold in the Dolphin East Load, Fiji; Proc. Aus., no. 141, pp. 21-46, 1946.

49. AFENYA, P. M., Studies in the processing of a carbonaceous gold ore; Ph.D. Thesis, Imperial College London, 1976.

50. MAINWARING, P. R., Process Mineralogy of gold ores- A review; Proceedings of the International Symposium on Gold Metallurgy, R. S. Salter, D. M. Wyslouzil and G. W. McDonald (eds.) pp. 23-34, 1987.

51. MAINWARING, P. R., Presented at the 24th CIM Annual Conference of Metallurgist, Vancouver, B.C. Canada, 1985.

52. CHRYSSOULIS, S. L., CABRI, L. J., and SALTER, R. S., Direct determination of invisible gold in refractory sulfide ores; Proceedings of the International Symposium on Gold Metallurgy, Winnnipeg, Canada, Pergamon Press, Oxford, pp. 235-244, 1987.

53. OSSEO-ASARE, K., AFENYA, P.M., and ABOTSE, G.M.K., Carbonaceous matter in gold ores: Isolation, characterization and adsorption in aurocyanide solution; Precious Metals: Mining, Extraction, and Processing, V. Kudryk, et al. (Editors), TMS-AIME, Warrendale, Pennsylvania, pp. 125-144. 1984.

54. CARNEJO, L. M., and SPOTTISWOOD, D. J., Fundamental Aspects of Gold Cyanidation Process: A Review; Mineral and Energy Resources, vol. 27, no. 2, pp. 1-8, March 1984.

55. STEFANAKIS, M., HASSAPIS, J., DEMETRIADES, D., and KONTOPOULOS, D., Dearsenifying roasting and gold extraction from a refractory pyrite concentrate; Arsenic Metallurgy Fundamentals and Applications, R. G. Reddy, et al. (eds.), pp. 173-197, 1988.

56. HENLEY, K. J., Gold-Ore mineralogy and its relation to metallurgical treatment; Minerals Science Engineering, vol. 7, no. 4, pp. 289-312, Oct. 1975.

57. MUIR, D. M., Carbon-in-pulp technology for the extraction of gold; Aust. Inst. Min. Met., Parkville, Australia, pp. 7-22, Dec. 1982.

58. ZADRA, J. B., A process for the recovery of gold from activated carbon by leaching and electrolysis; U.S. Bureau of the Interior, Report of Investigation no. 4672, 1950.

59. FELDTMANN, W. R., The precipitation action of carbon in contact with auriferous cyanide solutions; Trans. Inst. Min. Metall. 24, pp. 329-343. 1914/15.

60. AVERY, P. W., Precipitating action of carbonaceous shale in cyanide solution; Mining and Scientific Press, pp. 514-516, April 8, 1916.

61. FISHER, H., Effect of black slate on cyanidation; Mining and Scientific Press, pp. 743-745, May 20, 1916.

62. HAUSEN, D. M., Process Mineralogy of Select Refractory Carlin-Type Gold Ores; CIM Bulletin, 78, pp. 83-94, 1985.

63. HUTCHINS, S. R., BRIERLEY, J. A., and BRIERLEY, C. L., Microbial Pretreatment of Refractory Sulfide and Carbonaceous Gold Ores; Process Mineralogy VII: Applications to Mineral Beneficiation Technology and Mineral Exploration, with Special Emphasis on Disseminated Carbonaceous Gold Ores, pp. 53-66, 1987.

64. HAUSEN, D. M. and BUCKNAM, C. H., Study of Preg Robbing in the Cyanidation of Carbonaceous Gold Ores from Carlin, Nevada; Applied Mineralogy, AIME, New York, pp. 833-856, 1984.

65. OSMANSON, R. D., Gold occurrence and the effect of roasting temperature on cyanidation recovery from the Gold Acres deposit, Lander country, Nevada; Process Mineralogy VII, Application to Mineral Beneficiation Technology and Mineral Exploration, with Special Emphasis on Disseminated Carbonaceous Gold Ores, pp. 41-49, 1987.

66. GUAY, W. J., and PETERSON, D. G., Recovery of Gold from Carbonaceous ores at Carlin, Nevada; Trans. SME-AIME, vol. 245, pp.102-104, 1973.

67. VASSILIOU, A. H., Gold in disseminated carbonaceous ores; Journal of Metals, pp. 26-28, April 1988.

68. KING, A., Gold Metallurgy on the Witwatersrand , Trans. Chamber of Mines, South Africa, pp. 1-16, 1949.

69. ZUMBERGE, J. E., SIGLEO, A. C., and NAGY, B., Molecular and Elemental Analysis of the Carbonaceous Matter in the Gold and Uranium Bearing Vaal Reef Carbon Seams, Witwatersrand Sequence; Minerals Sci. Engng. vol. 10, no. 4, Oct 1978, pp. 223-245.

70. RADTKE, A. S., and SCHEINER, B. J., Studies of hydrothermal gold deposition (1) Carlin Deposit, Nevada: The role of carbonaceous materials in gold deposition; Economic Geology, vol. 65, no.2, March-April 1970, pp.87-102.

71. DEMOPOULOS, G. P., and PAPANGELAKIS, V. G., Recent advances in refractory gold processing; CIM Bulletin, vol. 82, no. 931, pp. 85-91, Nov. 1989.

72. QUADRIO, A. J., and KELLET, K. P., Recovery of gold from Lancefield arsenical sulfide ore; Proceedings of Austr. IMM, Perth and Kalgoorlie Branches, Regional conference on Gold Mining, Metallurgy, and Geology, pp. 159-169, Oct. 1984.

73. ARCHIBAD, F. R., Roasting Arsenical Gold Ores and Concentrates; The Canadian Mining and Metallurgical Bulletin, pp. 129-139, March 1949.

74. HAQUE, K. E., Microwave irradiation pretreatment of refractory gold concentrate; Proceedings of the Symposium on Gold Metallurgy, Pergamon Press, pp. 327-339, 1987.

75. MASON, P. G., PENDREIGH, R., WICKS, F. D., and KORNZE, L. D., Selection of the process flowsheet for the Mercur gold plant; Mining, Precious Metals: Extraction, and Processing, pp. 435-445, 1984.

76. ZHUCKOV, I. A., LODEISHCHIKOV, V. V., and SKOBEEV, I. K., Behavior of carbon during oxidizing roasting of carbonaceous gold-arsenic concentrates; Tsvet. Metal., vol. 41, no. 9, pp. 33-34, 1968.

77. McCLINCY, R. J., Unlocking refractory gold ores and concentrates; Journal of Metals, pp. 10-11, Sept. 1990.

78. STRATHDEE, B. A., and PIDGEON, L. M., Thermal Decomposition and Vapor Pressure Measurements on Arsenopyrite and on Arsenical Ore; The Canadian Mining and Metallurgical Bulletin, pp.883-887, Dec. 1961.

79. VELTMAN, H., and WEIR, D. R., Sherritt Gordons's Pressure Leaching Technology- Its Industrial Application; Hydrometallurgy '81, Symposium of the Society of Chemical Industry, Manchester, 30 June-3 July, 1981.

80. HOLMES, J. A., Recent experience in the application of Hydrometallurgical techniques; Hydrometallugy '81, Symposium of the Society of Chemical Industry, Manchester, 30 June - 3 July 1981.

81. HEDLEY, N., and TABACHNIK, H., Process for recovering precious metals from refractory source materials; U.S. Patent no. 2,777,764, Jan. 1957.

82. BEREZOWSKY, R. M. G. S., and WEIR, D. R., Pressure oxidation pretreatment of refractory gold; Minerals and Metallurgical Processing vol. 1, no. 1, pp. 1-4, 1984.

83. FAIR, K. J., SCHNEIDER, J. C., and VAN WEERT, G., Options in the Nitrox Process; Proceedings of the International Symposium on Gold Metallurgy, Pergamon Press, pp. 279-291, 1987.

84. VAN WEERT, G., FAIR, K. J., and SCHNEIDER, J. C., Prochem's NITROX process; CIM Bulletin, vol. 79, no.895, pp. 84-85, 1986.

85. FAIR, K. J., and VAN WEERT, G., Precious Metals 1989, B. Harris, ed., IPMI, Allentown, Penn., pp. 305-371, 1989.

86. BEATTIE, M. J. V., RAUDSEPP, R., FOO, K. A., and BALDERSON, G. F., Precious Metals 1989, B. Harris, ed., IPMI, Allentown, Penn., pp. 327-333, 1989.

87. BEATTIE, M. J. V., BALDERSON, G., and FOO, K., Proc. Perth Intl. Gold Conf., Randol Intl. Ltd. Golden, Col., 1988.

88. BEATTIE, M. J. V., RAUDSEPP, R., and ISMAY, A., Arseno / redox process for refractory gold ores; Processing of Complex Ores, Proceedings of the International Symposium, CIM, edited by G. S. Dobby and S. R. Rao, Halifax, pp. 431-439, 1989.

89. SILL, H. A., Process for treating complex ores; U.S Patent no. 2,951,741, Sept. 1960.

90. CHILTON, C. H., Leach Licks Arsenic Bugaboo in metal ore; Chemical Engineering, vol. 65, No. 1, pp. 80-82, 1958.

91. WHITE, L., Treating refractory Gold Ores; Mining Engineering, vol. 42, No. 2, pp. 168-174, Feb. 1990.

92. BHAKTA, P. N. H. and LEI, K. P. V., Alkaline Oxidation Pretreatment of a Low Grade Sulfide Gold Ore; Proceedings of the Symposium of GoldTech 4, Reno, Nevada, pp. 91-95, 1990.

93. BHAKTA, P., LANGHANS, J. W., and LEI, K. P. V., Alkaline Oxidation Leaching of Gold-Bearing Arsenopyrite Ores; Report of Investigation 9258, Bureau of Mines, 1989.

94. LAWRENCE, R. W. and BRUYNESTEYN, A., Biological pre-oxidation to enhance gold and silver recovery from refractory pyritic ores and concentrates; CIM Bulletin, vol. 76, no. 857, pp. 107-110, 1983.

95. LIZAMA, H. M., and SUZUKI, I., Bacterial leaching of a sulfide ore by Thiobacillus ferrooxidans and Thiobacillus thiooxidans, Part II. Column leaching studies; Hydrometallurgy vol. 22, pp. 301-310, 1989.

96. LAWRENCE, R. W. and MARCHANT, P. B., Comparison of Mesophilic and Thermophilic Oxidation System for the treatment of Refractory Gold Ores and Concentrates; Proceeding of the International Symposium, Warwick, pp. 359-374, 1987.

97. KELLY, D. P., Evolution of the understanding of the microbiology and biochemistry of the mineral leaching habitat, BioHydroMetallurgy, Proceedings of the International Symposium, Warwick, pp. 3-14, 1987.

98. KOMNITSAS, C. and POOLEY, F. D., Mineralogical characteristics and treatment of refractory gold ores, Minerals Engineering, vol. 2, no. 4, pp. 449-457, 1989.

99. LAWRENCE, R. W., Biotreatment of gold ores; Microbial Mineral Recovery, H. L. Ehrlich and C.L. Brierley (Eds.), McGraw-Hill Publishing Company, pp. 127-148, 1990.

100. TSENG, B. H. and WERT, C. A., TEM Analysis of Sulfur and Chlorine in Organic Concentrates from Carbonaceous Gold Ore; Process Mineralogy VII: Applications to Mineral Beneficiation Technology and Mineral Exploration, with Special Emphasis on Disseminated Carbonaceous Gold Ores, pp. 67-80, 1987.

101. ROY, M. M., Studies on Coal Maceral, IV. Chlorination of Exinite and Fusinite; Economic Geology, vol. 60, pp. 1404-1410, 1965.

102. SCHEINER, B. J., LINDSTROM, R. E., GUAY, W. J., and PETERSON, D. G.; Extraction of Gold form Carbonaceous Ores: Pilot Plant Studies, U. S. Bureau of Mines, RI 7597, 1972.

103. McDOUGALL, G.J., and HANCOCK, R. D., Gold complexes and activated carbon- A literature review; Gold Bull., vol, 14, no.4, pp. 138, 1981.

104. BAILEY, P. R., Application of Activated Carbon to Gold Recovery; The Extractive Metallurgy of Gold in South Africa, vol. 1, Edited by G. G. Stanley, The Chamber of Mines of South Africa, pp. 379-381, 1987.

105. BREWSTER, N. E., LENDRUM, F. C. and SALTER, R. S., A case for C.I.L: The Eden Roc Project, Ivory Coast, West Africa; Projects '88, 18th Hydrometallurgical Meeting, Edmonton, Alberta, Canada, paper no. 2, 1988.

106. FLEMING, C. A., Recovery of gold by resin-in-pulp at the Golden Jubilee Mine; Precious Metals '89, edited by M. C. Jha and S. D. Hill, pp. 105-119, 1989.

107. FLEMING, C. A., Some aspects of the chemistry of carbon-in-pulp and resin-in-pulp processes; Paper presented at the seminar on Carbon-in-pulp Technology for the Extraction of Gold, Kalgoorlie, The Australasian Inst. Min. Metall., pp. 415-440, 1982.

108. SMITH, I., HINCHLIFFE, W., HOSKING, J. W. and MUIR, D. M., Fouling studies on C.I.P carbons and prospects for gold recovery using ion-exchange resins; Project no. 35 Report, Western Australian Mining and Petroleum Research Institute, Perth, 1984.

109. RUANE, M., HINCHLIFFE, W., HOSKING, J. W. and MUIR, D. M., Carbon-in-pulp gold processing Technology; Report no. 2, Western Australian Mining and Petroleum Research Institute, Perth, 1983.

110. POTTER, G. M., Effects of clay content on carbon-in-pulp process; World Mining, pp. 33, July 1981.

111. LEE, A. F., BROWN, T. D., and LAXEN, P. A., The distribution of humic substances in the dumps and carbon-in-pulp plant circuits at Rand Mines Milling and Mining; Pro. Int. Conf. on Gold, Gold 100, vol. 2, Extractive Metallurgy of Gold, edited by G. E. Fivaz, South Africa Inst. Min. Metall., pp.367-382, 1986.

112. HOSKING, J. W., The recovery of gold from ores by ion exchange resins; Gold-Mining, Metallurgy and Geology, Perth and Kalgoorlie Branches Regional Conference, Kalgoorlie, W. A., Australia, pp. 127-139, 1984.

113. ZAKHAROV, E. I., RYABCHIKOV, B. E., RUDENKO, N. G., MIKHEEV, L. K. and BESKROVNY, B. E., Pilot plant tests of a pulsating adsorption column for extraction of gold from non-clarified solutions; Soviet J. of Non-Ferrous Metals, vol. 16, no. 3, pp.89-91, 1975.

114. HENDRIKSZ, A. R., Modification to the conventional NIMCIX system for different Industrial applications, Paper E2, Proc. Hydrometallurgy '81 symposium, Soc. Chem. Ind., London, 1981.

115. GREAVES, J. N., PALMER, G. R. and WHITE III, W. W., The recovery of gold from refractory ores by the use of Carbon-in-Chlorine leaching; Journal of Metals, pp. 12-14, Sept. 1990.

116. AVRAAMIDES, J., HEFTER, G. and BUDESELIC, C., The Uptake of gold from chloride solutions; Proceedings of the AusIMM, vol. 290, pp. 59-62.

117. HUGHES, H. C. and LINGE, H. G., The kinetics of gold loading from gold (III) chloride solution onto fresh activated coconut carbon; Hydrometallurgy, vol. 22 , pp. 57-65, 1989.

118. SEYMOR, D., and RAMADORAI, G., Rapid Oxidation of Refractory Gold-Bearing Ores by Intense 'Flash Chlorination' at Newmont Gold Company; Precious Metals '89, Warrendale, PA: TMS, pp. 165-178, 1989.

119. BARR, D. S., Chlorination Operations at Jerritt Canyon, Nevada; Process Mineralogy VII: Applications to Mineral Beneficiation Technology and Mineral Exploration, with Special Emphasis on Disseminated Carbonaceous Gold Ores, pp. 29-39, 1987.

120. STREAT, M., and NADEN, D., Ion exchange and sorption processes in hydrometallurgy, critical reports on Applied Chemistry vol. 19; Published for the Society of Chemical Industry by John Wiley and Sons, 1987.

121. GREEN, M., The effect of charcoal in gold bearing cyanide solution with reference to the precipitation of gold; Trans. Inst. Min. Metall., vol. 23, pp. 65, 1913.

122. EDMONDS, H. R., The application of charcoal to the precipitation of gold from its solution in cyanide; Trans. Inst. Min. Metall., vol. 27, pp. 277, 1917.

123. ALLEN, A. W., Charcoal precipitation of aurocyanide; Metall. Chem. Engng, vol. 18, pp. 642, 1918.

124. WILLIAMS, L. B., Precipitation of gold from cyanide solutions by means of charcoal; Min. Mag. (Lond.), vol. 23, pp. 139, 1923.

125. GROSS, J. and SCOTT, J. W., Precipitation of gold and silver from cyanide solution on charcoal; U.S. Bureau of Mines Technical Paper No. 378, Washington, D.C, 1927.

126. GARTEN, V. A. and WEISS, D. E., The ion and electron exchange properties of activated carbon in relation to its behavior as a catalyst and adsorbent; Rev. Pure Appl. Chem., vol. 7, pp. 69, 1957.

127. KUZMINYKH, V. M. and TYURIN, N. G., The effect of acidity of a cyanide solution on adsorption of gold on carbon; Tsved. Metall., vol. 11, no. 4, pp. 65, 1968.

128. CHO, E. and PITT, C. H., The adsorption of silver cyanide on activated charcoal; Metall. Trans. IMM, 10B, pp. 159-169, 1979.

129. ANDERSON, T. N. and BOCKRIS, J. O. M., Forces involved in the specific adsorption of ionic metals from aqueous solution; Electrochim. Acta, vol. 9, no. 4, 1964.

130. FLEMING, C. A., and CROMBERGE, G., The extraction of gold from cyanide solution by strong- and weak-base anion-exchange resins; J. S. Africa Inst. Min. Metall. vol. 84, no. 5, pp. 125-137, May 1984.

131. ROBERTS, S. and STARKEY, J., Modernization of the Campbell Red Lake Mill in 1987; Proceedings of the International Symposium on Gold Metallurgy, 26th Annual Conference of Metallurgists of the CIM, Winnipeg, Manitoba, pp. 185-197, August 1987.

132. CONNELL, L. J. and CROSS, B. C., Roasting process at the Giant Yellowknife (Arsenic) Mine; 20th Annual Conference of Metallurgists of the CIM, Hamilton, Ontario, paper 13.3, August 25, 1981.

133. DJINGHENZIAN, L. E., Theory and Practice of Roasting Sulfide Concentrate, with special reference to Canadian gold ores and concentrates; Canadian Mining and Metallurgical Bulletin, pp. 352-361, June 1952.

134. COLLINS, M. J., BEREZOWSKY,R. M. and WEIR, D. R., The behavior and control of Arsenic in the pressure oxidation of Uranium and Gold feedstocks; Arsenic Metallurgy Fundamentals and Applications, TMS Annual Meeting, Phoenix, Arizona, pp. 115-133, 1988.

135. EACOTT, J. G., Considerations in controlling sulfur dioxide emissions from copper smelter; Copper Smelting- An Update, Proceedings of a Symposium sponsored by the Pyrometallurgical committee of The Metallurgical Society of AIME, at the 111th AIME Annual Meeting, edited by D. B. George and J. C. Taylor, Dallas, Texas, pp. 77-142, Feb. 1982.

136. LYNCH, D. C., A review of the physical chemistry of Arsenic as it pertains to primary metals production; Arsenic Metallurgy Fundamentals and Application, Proceedings of a Symposium Sponsored by the TMS-AIME, edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, pp. 3-33, Jan. 1988.

137. NISHIMURA, T., ITOH, C. T., and TOZAWA, K., Stabilities and Solubilities of Metal Arsenic and Arsenates in Water and effect of Sulfate and Carbonate ions on their Solubilities; Arsenic Metallurgy Fundamentals and Applications, edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, pp. 77-98, 1988.

138. MIRZA, A. H., TAHIJA, D., CHEN, K. and HAUNG, H. H., Formation and stability studies of Iron-Arsenic and Copper-Arsenic compounds from Copper Electrorefining sludge; Arsenic Metallurgy Fundamentals and Applications, edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, pp. 37-58, 1988.

139. NISHIMURA, T., ITOH, C. T., TOZAWA, K. and ROBINS, R. C., The Calcium-Arsenic-Water-Air System; Impurity-Control and Disposal, CIM 15th Annual Hydrometallurgical Meeting, paper no. 2, pp. 1-19, Aug. 1985.

140. KRAUSE, E., and ETTEL, V. A., Ferric Arsenate Compounds-Are They Environmentally Safe? Solubilities of Basic Ferric Arsenates; Paper in Impurity Control and Disposal, Proc. 15th CIM Annu. Hydrometall. Meet., Vancouver, British Columbia, Canada, paper no. 5, pp. 1-20, 1985.

141. ROBINS, R. G., The Aqueous Chemistry of Arsenic in Relation to Hydrometallurgical Processes; Paper in Impurity Control and Disposal, Proc. 15th CIM Annu. Hydrometall. Meet., Vancouver, B. C., Canada, paper no.1, pp. 1-26, 1985.

142. Powder Diffraction File Inorganic Phases Search Manual, (Hanawalt) JCPDS, Published by the International Centre for Diffraction Data, U. S. A, 1988.

143. Selected Powder Diffraction Data for Minerals, first edition, Published by the Joint Committee on Powder Diffraction Standards, U. S. A, 1974.

144. BUGBEE, E. E., A Testbook of Fire Assaying, Colorado School of Mines Press, Golden, Colorado, Third edition, 1983.

145. BACON, W. G., HAWTHORN, G. W., and POLING, G. W., Gold Analysis - Myths, Frauds and Truths, CIM Bulletin, vol. 82, no. 931, pp. 29-36, 1989.

146. FURMAN, N. H., Standard Methods of Chemical Analysis, N. H. Furman (editor) Sixth edition, vol. 1, D. Van Nostrand Company Inc, 1966.

147. OTAIGBE, J. U. and EGIEBOR, N. O., Athabasca Petroleum Coke Utilization: Coagglomeration with Sulfur Sorbents for control of Sulfur Dioxide Emissions during Combustion; Energy and Fuels, no. 5, pp. 30-34, 1991.

148. PERRY, R. H. and GREEN, D., Chemical Engineer's Handbook; McGraw-Hill, New York, pp. 9-43 - 9-48, 1984.

149. ARRIAGADA, F. J. and OSSEO-ASARE, K. , Gold extraction from refractory ores: Roasting behavior of Pyrite and Arsenopyrite, Precious Metals: Mining, Extraction, and Processing. (eds.) V. Kudryk, D. A. Corrigan and W. W. Liang, pp. 367-385, 1984.

150. STEFANAKIS, M. and KONTOPOULOS, A., Production of Environmental Acceptable Arsenites-Arsenates from solid Arsenic Trioxide; Arsenic Metallurgy Fundamentals and Applications, edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, pp. 287-304, 1988.

151. NISHIMURA, T. and TOZAWA, K., Removal of arsenic from waste water by addition of calcium hydroxide and stabilization of arsenic-bearing precipitate by calcination; Impurity Control and Disposal, Proceedings of the 15th Annual Hydrometallurgical Meeting of CIM, Vancouver, Canada, paper no. 3, pp. 1-8, Aug. 18-22, 1985.

152. BARTLETT, R. W. and HAUNG, H. H., The Lime-Concentrate-Pellet Roast Process for treating Copper Sulfide Concentrates; Journal of Metals, pp. 28-34, Dec. 1973.

7. APPENDIX

DATA USED IN FIGURES

Figure 10

Pressure (Kpa)	% S oxidation	% C oxidation	% Au extraction	% Au extraction
1000	0.8	0.7	63.0	66.0
1500	2.3	1.0	69.0	66.0
2000	5.4	1.3	72.0	75.0
2500	7.1	1.8	75.0	72.0
3000	7.9	2.9	75.1	74.3

Figure 11

Pressure (Kpa)	% S oxidation	% C oxidation	% Au extraction	% Au extraction
1000	1.1	2.9	69.0	68.0
1500	6.8	3.9	70.0	71.9
2000	9.3	4.5	72.5	71.0
2500	15.0	5.0	74.0	72.4
3000	20.4	6.1	76.0	73.2

Figure 12

Pressure (Kpa)	% S oxidation	% C oxidation	% Au extraction	% Au extraction
1000	1.4	2.9	68.5	66.4
1500	7.1	4.2	70.5	72.4
2000	11.9	3.9	72.6	70.0
2500	19.8	6.4	75.8	75.0
3000	7.9	6.1	74.5	73.6

Figure 13

% Solids	% S oxidation	% C oxidation	% Au extraction	% Au extraction
30	19.8	6.1	71.5	73.6
20	22.9	6.6	74.0	72.2
10	30.6	7.2	75.0	77.0

Figure 14

Temp. °C	% S oxidation	% C oxidation	% Au extraction	% Au extraction
130	13.0	6.1	67.3	65.3
180	89.5	9.8	71.5	70.0
200	92.4	14.7	70.0	72.0

Figure 15

pH	% S oxidation	% C oxidation	% Au extraction	% Au extraction
1.0	92.9	14.0	67.8	69.7
1.5	92.4	14.7	70.0	69.8
2.0	75.5	10.1	69.2	67.2
2.5	41.9	9.6	70.5	72.6

Figure 16

Time (min.)	% S oxidation	% C oxidation	% Au extraction	% Au extraction
30	85.2	10.9	73.0	75.0
60	92.4	14.7	70.0	69.2
90	94.6	14.7	69.5	68.2
120	95.5	13.5	63.9	65.2

Figure 17

Time (min.)	% S oxidation	% C oxidation	% Au extraction	% Au extraction
30	86.1	9.3	63.9	62.5
60	90.4	13.6	60.1	62.0
90	94.6	14.6	65.7	64.3
120	96.8	14.9	64.8	65.5

Figure 18

Time (min.)	% S oxidation	% C oxidation	% Au extraction	% Au extraction
30	9.3	6.2	71.7	69.2
60	26.3	9.3	83.2	81.1
90	45.7	10.6	80.3	82.5
120	68.3	11.8	83.5	80.3

Figure 19

Residues	% S oxidation	% C oxidation	% Au extraction
Roast	80.2	98.0	95.1
Peroxide	68.3	11.8	83.5
Sulfuric	95.5	13.5	63.9
Nitric	96.8	14.9	64.8

Figure 20

Time (min.)	Untreated	Sulfuric	Nitric	Peroxide	Roasted
0	25.00	25.00	25.00	25.00	25.00
5	3.45	12.15	15.45	14.65	25.00
10	2.35	10.55	14.50	13.10	24.90
20	1.50	8.45	11.95	12.55	24.92
40	0.60	7.00	10.00	11.75	24.83
60	0.40	6.05	7.85	10.25	24.71
90	0.40	4.60	5.70	8.85	24.70
120	0.30	3.70	4.00	7.80	24.50
150	0.30	2.50	2.85	6.50	24.1
180	0.20	-	-	-	-
270	-	1.50	1.30	5.30	24.10
300	0.20	-	-	-	-
360	0.20	0.80	0.75	4.30	24.00

Figure 21

Time (hrs)	Roasted	Peroxide	Sulfuric	Nitric	Untreated
0.0	0.0	0.0	0.0	0.0	0.0
0.5	58.6	56.9	52.1	35.3	49.1
1.0	69.8	62.5	53.2	44.5	50.7
2.0	73.6	64.4	56.3	47.6	52.2
3.0	76.4	65.5	57.4	52.2	52.5
5.0	83.7	68.2	58.5	53.7	52.5
6.0	83.7	68.2	59.6	56.8	52.9
10.0	86.5	71.1	62.7	59.9	53.3
12.0	87.9	71.1	64.9	60.3	52.8
23.0	89.5	80.2	67.9	63.0	55.3
25.0	92.3	82.4	69.1	64.9	55.3
28.0	95.1	83.9	70.3	66.0	55.3

Figures 22-26

Temp. (°C)	% S capture Ca/S = 0.5	% S capture Ca/S = 1.0	% S capture Ca/S = 1.5	% S capture Ca/S = 2.0
500	38.7	67.3	87.5	92.9
600	42.3	77.7	91.4	96.9
700	43.8	80.6	94.9	96.3
800	40.4	80.4	93.7	96.1

Figures 27-31

Temp. (°C)	% As capture Ca/S = 0.5	% As capture Ca/S = 1.0	% As capture Ca/S = 1.5	% As capture Ca/S = 2.0
500	27.7	51.0	53.7	58.3
600	72.0	76.6	76.6	78.9
700	74.1	81.3	84.4	84.2
800	25.1	47.4	68.9	67.2

Figure 32

Temp. (°C)	% C oxidation	% C oxidation	% C oxidation
500	36.6	38.2	39.0
600	89.5	87.3	85.5
700	97.3	95.2	94.7
800	99.3	97.4	96.8

Figure 33

Temp. (°C)	% Au extraction	% Au extraction	% Au extraction
500	76.0	74.5	77.5
600	90.5	89.5	91.5
700	95.6	94.5	96.4
800	90.3	89.8	91.4

Figure 34

Ca:S mole ratio	% Au extraction (500°C)	% Au extraction (500°C)	% Au extraction (500°C)
0.0	76.0	77.5	74.5
0.5	72.4	71.5	73.3
1.0	67.0	66.8	67.2
1.5	63.6	64.5	65.1
2.0	66.3	67.8	65.5

Figure 35

Ca:S mole ratio	% Au extraction (600°C)	% Au extraction (600°C)	% Au extraction (600°C)
0.0	90.5	91.5	89.5
0.5	82.2	81.8	83.4
1.0	83.5	82.3	84.2
1.5	79.2	78.5	80.0
2.0	75.9	74.8	76.0

Figure 36

Ca:S mole ratio	% Au extraction (700°C)	% Au extraction (700°C)	% Au extraction (700°C)
0.0	95.6	96.4	94.5
0.5	96.3	95.8	96.7
1.0	95.4	95.0	96.1
1.5	92.3	93.0	91.8
2.0	92.9	92.5	93.2

Figure 37

Ca:S mole ratio	% Au extraction (800°C)	% Au extraction (800°C)	% Au extraction (800°C)
0.0	90.3	91.4	89.8
0.5	88.5	87.6	89.8
1.0	83.4	84.1	83.0
1.5	68.1	68.5	70.2
2.0	79.3	80.1	78.5

Figure 38

Ca:S mole ratio	% As in solution (500°C)	% As in solution (500°C)	% As in solution (500°C)
0.0	9.8	10.8	8.8
0.5	7.2	6.4	9.1
1.0	3.4	4.2	5.9
1.5	4.2	1.7	2.5
2.0	0.9	1.7	0.9

Figure 39

Ca:S mole ratio	% As in solution (600°C)	% As in solution (600°C)	% As in solution (600°C)
0.0	9.2	12.4	8.2
0.5	6.6	9.8	5.7
1.0	6.5	9.7	5.6
1.5	2.4	4.8	4.0
2.0	8.8	2.4	4.0

Figure 40

Ca:S mole ratio	% As in solution (700°C)	% As in solution (700°C)	% As in solution (700°C)
0.0	6.4	6.4	5.3
0.5	4.3	1.7	1.7
1.0	1.6	0.8	4.0
1.5	2.4	3.9	5.5
2.0	5.0	2.5	4.2

Figure 41

Ca:S mole ratio	% As in solution (600°C)	% As in solution (600°C)	% As in solution (600°C)
0.0	2.7	2.7	2.7
0.5	2.5	3.4	1.7
1.0	2.4	0.8	0.8
1.5	3.2	0.8	3.2
2.0	3.3	2.5	1.7